Biomass thermal conversion. Pelletisation of lignocelluloses and the effect on the gasification process

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PhD Thesis

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Abstract

Agricultural residues and energy crops constitute an important part of the energy chain although they are not being used extensively in the energy generation processes since they are associated with disadvantages such as low bulk and energy densities and handling problems. One solution is the pelletisation of these residues, which solves a great deal of these problems and enables the competition of biomass with other types of fuels. A large amount of work, concerning the combustion of biomass pellets, has been done previously, however, studies on biomass pellet gasification are still limited. An effort is made, in the current project, to connect the pelletisation and the gasification processes so that the work presented here could constitute a guide to the industry.

The quality of the pellets to be gasified is affected by the initial pelleting parameters, namely the feedstock moisture content, the feedstock particle size and the die diameter. These parameters in turn, affect the process of gasification. These relationships were studied with the purpose of finding an optimum behaviour in the pelleting process that would allow high efficiencies of pellet gasification. The agricultural residue investigated was oilseed rape due to high cultivation in the UK. Oilseed rape straw (OSRS) was pelletised and used in two types of gasifiers; a downdraft and a spouted fluidised bed gasifier. Other types of biomass pellets such as Miscanthus pellets and Dried Distillers Grains with Solubles (DDGS) pellets were also studied. The gasification performance of the OSRS pellets was compared with the performance during gasification of Miscanthus and DDGS pellets.

The results showed that dry and large pellets required more energy to be manufactured than the wet and small pellets. In addition, the results revealed the connection of the initial pelleting parameters and the quality of pellets which was assessed in terms of the pellet density, the bulk density and the pellet durability. The wet pellets with a small particle size had the highest density and the dry pellets had the highest bulk density and durability.

The effect of the initial pelleting parameters on the gasification was also studied. It was found that the high feedstock moisture content negatively affected the gasification performance in both downdraft and spouted fluidised bed gasification. The feedstock particle size did not have an effect on the downdraft gasification but a minor effect was identified for the spouted fluidised bed. Large pellets were unable to be processed in the downdraft gasifier due to the increased bed porosity and pellet density and decreased amount of active carbon sites, while both large and small pellets were successfully processed in the spout bed gasifier. The gas higher heating value (HHV) produced in gasification was typically quite low, of between 2-4 MJ/m^3.

The comparison of the pellets showed that Miscanthus pellets had the highest gasification performance followed by the dry OSRS pellets, the wet OSRS pellets and finally the DDGS pellets. The most important reason for these differences was identified to be the ash content of the pellets.

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List of abbreviations

CCE: Carbon Conversion Efficiency

CGE: Cold Gas Efficiency

CHP: Combined Heat and Power

DD: Die Diameter

DDGS: Dried Distillers Grains with Solubles

ER: Equivalence Ratio

HCE: Hydrogen Conversion Efficiency

HHV: Higher Heating Value

IGCC: Integrated Gasification Combined Cycle

LHV: Lower Heating Value

MC: Moisture Content (feedstock)

MTOE: Million Tonnes of Oil Equivalent

OCE: Oxygen Conversion Efficiency

OSRS: Oilseed Rape Straw

PS: Particle Size (feedstock)

SD: Standard Deviation

SRC: Short Rotation Coppice

Energy equivalents

1 kWh	=	3.6 MJ
1 MTOE	=	11.63 TWh or 11,630,000,000 kWh
	=	41,868 TJ or 41,868,000,000 MJ

1 Introduction

1.1 Renewable energy in UK and the world

Energy is one of the great pillars in the ascent of Man. Humans were always finding comfort and warmth around the fire, they used it for food and to protect themselves. Nowadays, energy is used in all forms for all kinds of uses but this special relationship between Man and energy was always the same.

Due to many reasons, some which will be discussed later on, it became of vital importance to make use of renewable energies from sources such as solar, wind, wave, tidal and biomass energy. This became apparent as fossil fuels, especially oil, exist in finite quantities. The independence from reliance on fossil fuels is also independence from interests that control these resources. Due to this, the decision making process is highly political but also social.

One important source of renewable heat and power is biomass. The biomass sources vary depending on the location and the policies with wood and agricultural residues being amongst the most abundant biomass sources.

The total available wood in Europe is in the region of 25 billion m^3, of which 530 million m^3 are used annually. Around 55% (290 million m^3) is used in various wood products and 45% (240 million m^3) is used for energy generation. The 240 million m^3 corresponds to 75 MTOE (Mega tonnes of oil equivalent) or to 528 MWh or to 1920 GJ [1]. In the UK the largest amount of wood flows (80% of the total), which includes the wood-derived products is retrieved from recovered paper and the saw mill industry [1]. Furthermore, the UK wood imports are larger than the UK exports with less than 0.5% share on the total UK GDP [1].

There are, obviously, other forms of biomass available in Europe and UK apart from wood. Figure 1.1 shows the percentage of the various biomass resources available in EU-24 and Norway (2006 statistics). It is clear that the major sources of biomass in Europe are the herbaceous and fruit-derived biomass, the forest residues and those produced for firewood. For the UK, the position is different due to the lack of forests. So, the major source of biomass in the UK is the herbaceous and fruit-derived biomass followed by used wood, wood retrieved from waste and also other biomass, which equate to more than 300 PJ availability in the UK (of total 6,500 PJ in Europe) [2].

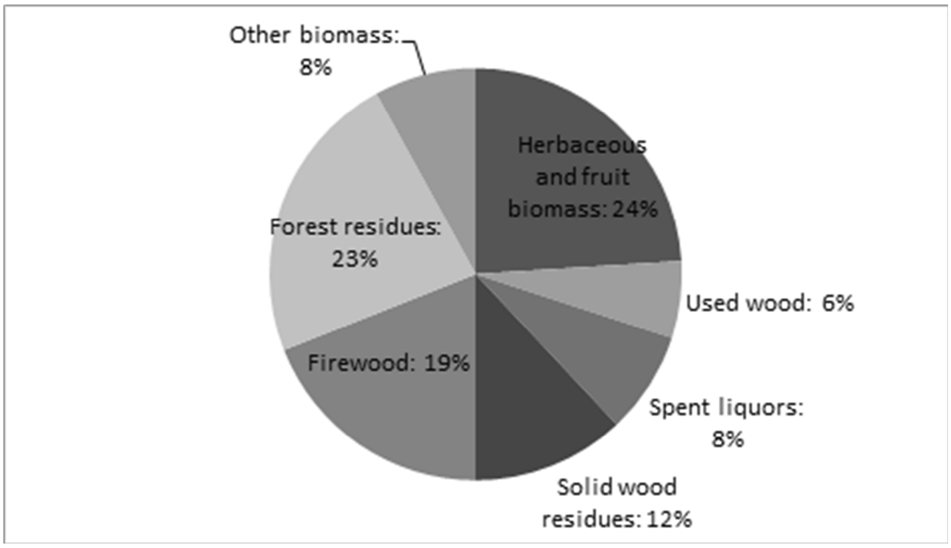

Figure 1.1: Biomass resources in EU-24 and Norway [2].

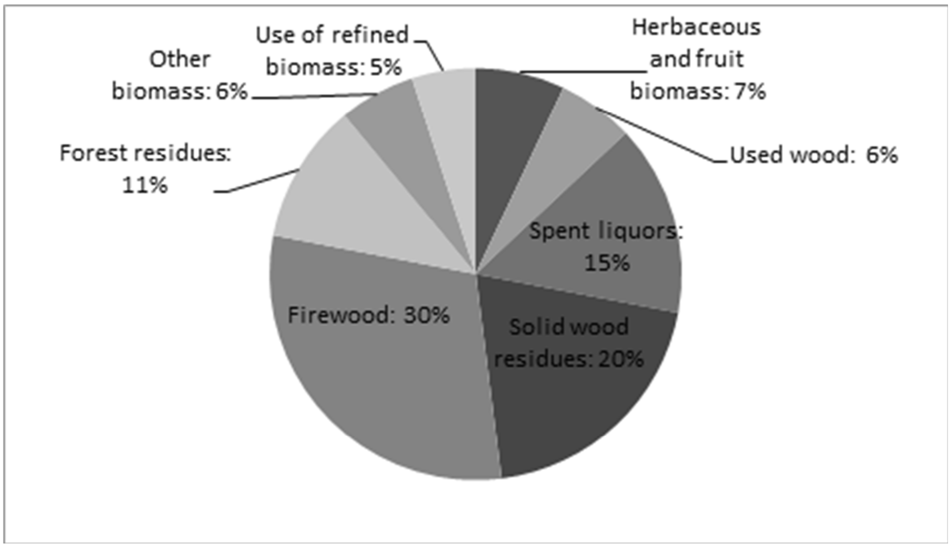

Figure 1.2: Biomass use in EU-24 and Norway [2]

Table 1.1: Total availability and biomass use in Europe in 2006 [2]

Biomass resources in Europe	**Biomass Availability (2006)**		**Biomass use (2006)**		**Percentage use (%)**
	MTOE	PJ	MTOE	PJ	
Herbaceous and fruit biomass	38	1582	6	232	15
Forest residues	35	1461	8	340	23
Firewood	29	1224	22	937	77
Solid industrial wood residues and by-products	22	901	19	809	90
Other biomass	13	559	5	193	35
Spent liquor	12	482	12	482	100
Used wood	9	368	4	183	50
TOTAL	157	6,577	76	3178	48

Figure 1.2 and Table 1.1 show the major biomass sources that are used in Europe which are firewood, industrial wood residues and spent liquor. On the contrary the total biomass use in UK in 2006 was a little more than 60 PJ with major contributors the forest residues and the industrial wood residues (50 PJ together) followed by used wood and refined biomass [2].

The share of biomass and wastes in the gross inland energy consumption increased in the EU-27 from 3-3.5% to nearly 5.5% from 1996 to 2007. Around 70% of the biomass and wastes is woody biomass, but is expected to decrease as other forms of biomass are utilised such as herbaceous crops [3]. 2008 statistics, show that biomass and wastes share in energy consumption in UK is amongst the lowest in Europe with less than 2.5%. This is only higher than Ireland, Cyprus, Malta and Iceland [3] while the potential throughout the whole Europe is definitely higher (Table 1.2) [2].

Table 1.2: Biomass potential in Europe [2]

	2010 (in PJ)	**2030 (in PJ)**
Energy crops	800	6,000
Forestry and forest residues	1,000	900
Agricultural residues and organic waste	2,900	3,100
TOTAL	4,700	10,000

The available arable land in UK for the cultivation of bioenergy crops is 824,000 hectares with the potential to grow to 1,118,000 hectares in 2020 and 1,584,000 hectares in 2030. In the EU-22 the numbers are: 12,965,000 in 2010, 16,170,000 in 2020 and 19,267,000 in 2030 [4]. This means that the bioenergy potential due to the agriculture and waste is high in the UK (Table 1.3).

Table 1.3: Environmentally-compatible bioenergy potential in UK (MTOE), agricultural residues belong to “waste” [4]

	2010	**2020**	**2030**
Agriculture	3.4	8.8	14.7
Forestry	1.5	1.5	1.1
Waste	8.6	8.7	8.6
TOTAL	13.5	19	24.5

In the UK, the major barriers concerning the biomass use are the raw materials supply, the sustainability concerns and the competition with fossil fuels. Scarcity of wood as reported by the UK is the major market barrier for trading pellets [2]. This is shown also by the large imports especially from Canada. The share of the Canadian wood pellet imported to the UK was high in 2008; 39% of Canadian wood pellets ended up in the UK markets. The other major Canadian wood pellet exports were to the Netherlands 37%, Belgium 21% and Sweden 3% [3]. UK imports large quantities of biomass products for energy production. For the year 2005-2007, plant-based biomass (straw, SRC etc), which was the second largest source of biomass source of energy, utilised 40% of imported material; landfill gas was the primary source of biomass energy [5].

In Europe, only Latvia has enough raw materials to be self-sufficient in the wood pellet production. **For this reason it is important to consider alternative biomass resources and their implementation into the end-user market.**

A very important agricultural crop is the oilseed rape. The production of oilseed rape in the EU-25 had reached in 2005 the 15.5 million tonnes which is a nearly 30% higher compared to 5 years previously. The oilseed rape that year, grew in 4.8 million hectares of which the nearly 80% is concentrated in 5 countries as it can be seen in the Table 1.4 [6].

Table 1.4: Oilseed rape production in various European countries [6]

	Hectares (million)	**% of total in Europe**
Germany	1.35	28.1
France	1.21	25.2
UK	0.6	12.5
Poland	0.55	11.5
Czech Republic	0.27	5.6
TOTAL (of five countries)	3.98	82.9

The total area of arable land in UK from the year 2006 to 2010 for various crops is shown in Figure 1.3. The graph clearly shows that oilseed rape is an important crop for the British agriculture as it is the third largest cultivated crop in UK after wheat and barley [7].

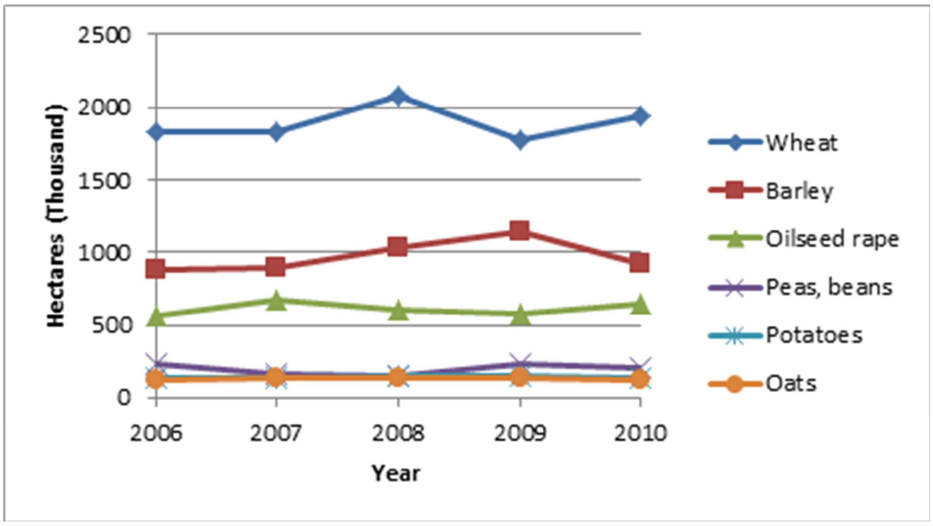

Figure 1.3: Arable land for various crops in UK [7]

Currently, in the UK, 0.2 million tonnes of straw (derived from various cereals and oilseed rape) are used in various thermal processes (2008 data), but at the same time, more than 10 million tonnes of straw are available (Table 1.5). As a comparison, 3 million dry tonnes of cereal straw is about 1 MTOE and in energy terms 40,000 to 50,000 TJ [5]. To help understand the analogies, 1 MTOE corresponds to electrical power supply for more than 700,000 medium size houses (assuming that transformation efficiency of thermal power to electricity is 0.2 which is a conservative estimation)[1].

Table 1.5: Arable land and straw production for various crops in the UK [5]

Crop	**Ha**	**Straw production (t/ha)**
Wheat	2,000,000	3.75
Barley	1,000,000	2.75
Oilseed rape	500,000	1.5
Oats	100,000	
Triticale	13,000	
Rye	9,000	

Despite the high potential of the energy crops such as Miscanthus, Switchgrass, Reed canary grass, Willow and Poplar, the current use is very low; less than 15 thousand hectares for Miscanthus and willow combined (data of 2009) [5].

[1] Calculated under the assumption that the average electricity consumption of a medium-scale household in the UK is 3,300 kWh/y [8]

Biomass electricity

Currently the contribution of renewables in the UK electricity production is 5% of which the 80% comes from bioenergy. Agricultural and wood residues and biogas were the main support in bioenergy supply. On the contrary, less than 0.1% of total electricity produced using energy crops and short rotation coppice (using 2009 data). Concerning the heat demand, biomass contributes with less than 1%. In general, 2006 statistics indicate that straw or wood products contribute approximately 6.3 TWh of heat energy to the non-residential markets [5].

Thus, renewable energy could contribute to further 10% (to reach 15%) in the total electricity production as it is required by the UK Renewables Obligation (15% of electricity must be derived from renewable by the year 2020) [9, 10].

The production of primary renewable energy in the UK in 1997 was 2.071 MTOE of a total 92.39 MTOE in EU-27. The production in UK in 2007 increased to 4.368 MTOE of a total 138.831 MTOE. The share of various renewable primary sources was (2007) 1.1% solar, 78.5% biomass, 10% hydropower and 10.4% wind energy [11].

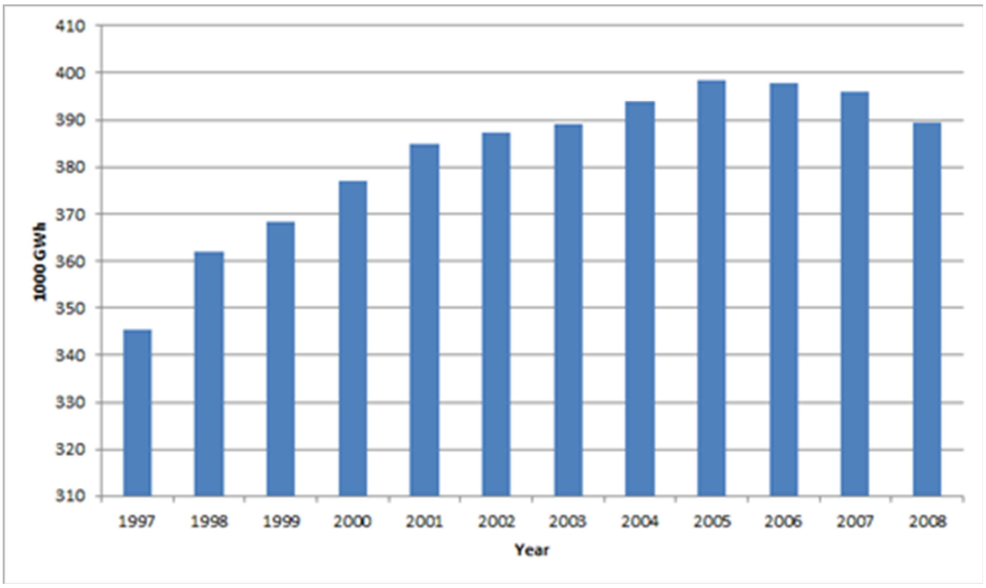

Figure 1.4: Electricity generation trends in UK [11, 12]

Figure 1.4 shows the gross electricity generation in the UK which is the electricity *measured at the outlet of the main transformers.* The proportion of electricity in UK that was generated from renewable sources was about 5% in 2007 to reach 10% in 2010 (in terms of the gross electricity consumption) [11]. In Figure 1.5 the amount of electricity that each fuel has contributed to the UK can be observed.

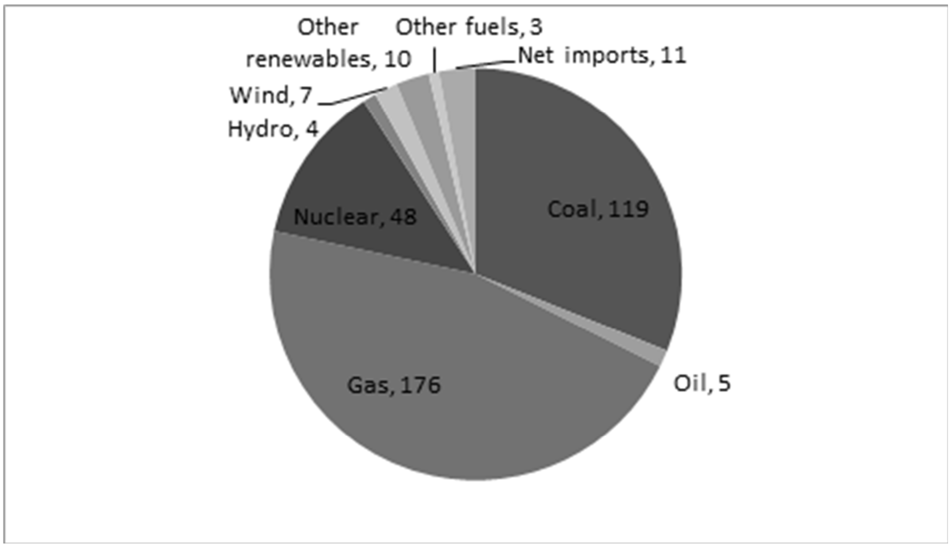

Figure 1.5: The UK electricity supply in 2008 in TWh [13]

Total electricity supplied in the UK in 2007 was **378 TWh** which is equal to 1.36 EJ ($1.36x10^{18}$ J). In 2008 the quantity was expected to rise. Out of the total electricity supply, **31.4 TWh** or 113.1 PJ ($113.1x10^{15}$ J) or the 8.3% was produced using biomass and more specifically in Table 1.6 [13]:

Table 1.6: Electricity generation from various biomass sources in UK [13]

Electricity generation, source 2007	**PJ**
Landfill gas	64.22
Straw, SRC, and other plant based biomass	32.47
Poultry, litter, meat and bone and other farm waste	9.32
Sewage gas	7.1
TOTAL	113.1

3.6 PJ = 1 TWh or 3.6 MJ = 1 kWh

Electricity in UK is produced mainly by gas, coal and nuclear means (45, 28 and 18% respectively). The renewables are responsible only for the 7% of total electricity production [14]

In 2009, 37% of renewable electricity was generated using onshore and offshore wind technology. In the same year the biomass contribution to electricity production was 22% (co-firing and other biomass) but without including the landfill gas (another 20%). The total amount of electricity generated from renewable sources was 10 TWh in the year 2000, and was increasing gradually ever since to reach 25 TWh (total of 372 TWh) in the year 2009 [14].

The electricity generated from renewable sources has been growing since the year 2000, in which the renewables contributed to the 2.5% of the total electricity generated to reach about 7% in the year 2009 [14].

On the other hand the potential of certain biomass sources in UK is much higher [13]:

Table 1.7: Potential of various biomass sources in the UK [13]

Biomass sources	**TWh**	**PJ**
Fuel wood (forest)	13	46.8
Straw	14.5	52.2
Wood waste	26	93.6
Waste (municipal/industrial)	15.5	55.8
Agricultural waste	10	36
Energy crops	17.2	61.92
TOTAL	96.2	346.32

The information above means that **the biomass potential is 3 times larger than the current supplied biomass for electricity**.

1.2 Pellets in UK: History and today

Pellet production in the UK started in 2002 with the Wales biofuel centre and a production capacity of 10,000 tonnes/y using wood. Similarly, another plant during the same year, Durham (Premier Waste) using waste wood was pelletising at the rate of 3.5 tonnes/hour. Since then the production capacity have grown substantially: 25,000 tonnes in 2005, 83,000 tonnes in 2006, 104,000 tonnes in 2007 and 218,000 tonnes in 2008 [15].

The amount of pellets produced in UK in the year 2010 was 138,000 tonnes out of the 9,241,000 tonnes in the entire EU. Accordingly the pellet capacity in UK was 218,000 tonnes while in EU was 14,845,000 tonnes. 499 pellet producers are recorded in EU, 15 of them are in the UK [16].

The pellet imports to the EU (from outside EU) in 2009 and 2010 were 1,771,000 and 2,523,000 tonnes respectively indicating a 70% increase. Similarly, the internal imports were increased from 2,164,000 in 2009 to 3,445,000 tonnes in 2010 showing an increase of 63% [16]. Similarly, in UK, the pellet imports from outside EU increased from 3,000 in 2009 to

511,000 tonnes in 2010 (mainly from Canada and USA) while the imports from within the EU slightly decreased from 42,000 in 2009 to 40,000 tonnes in 2010 [16].

The amount of pellets consumed in UK in the year 2010 was 176,000 tonnes, while the total consumption in the EU was 9,187,000 tonnes [16].

In overall, the pellet production in the UK constitutes the 1.5% of the total EU production, while the consumption in UK constitutes the 1.9% of the total EU consumption [16].

Pellet prices are comparable with other fuels as we can see in Table 1.8. Especially for UK, the wood pellet prices dropped from 13 €/GJ in 2007 to about 10.5 €/GJ only to increase again to 12 €/GJ (or 200 €/tonne) by the end of 2009. Furthermore prices of pellets for domestic use are different than prices of pellets for industrial use. An example: The bulk pellet price in Sweden is slightly more than 200 €/tonne. The pellet prices delivered in small bags are slightly smaller, nearly 230 €/tonne. But the wood pellets for industrial use is sold for less than 150 €/tonne [17].

Table 1.8: Fuel prices between the years 2007-2009 [17]

Fuel	**Price (€/GJ)**
Wood pellets	6-8
Coal	2-5
Ethanol	15-20
Gasoline	25-30
Crude oil	5-15
Diesel	10-20
Rapeseed oil	15-30

1.3 UK requirement to exploit renewables

The UK oil and gas reserves are declining at a rate of 5% per annum at the best case scenario decreasing from 3 million barrels of oil equivalent per day in 2007 to around 1 million in 2028. Another scenario predicts less than 0.5 million barrels of oil equivalent in 2028 [18].

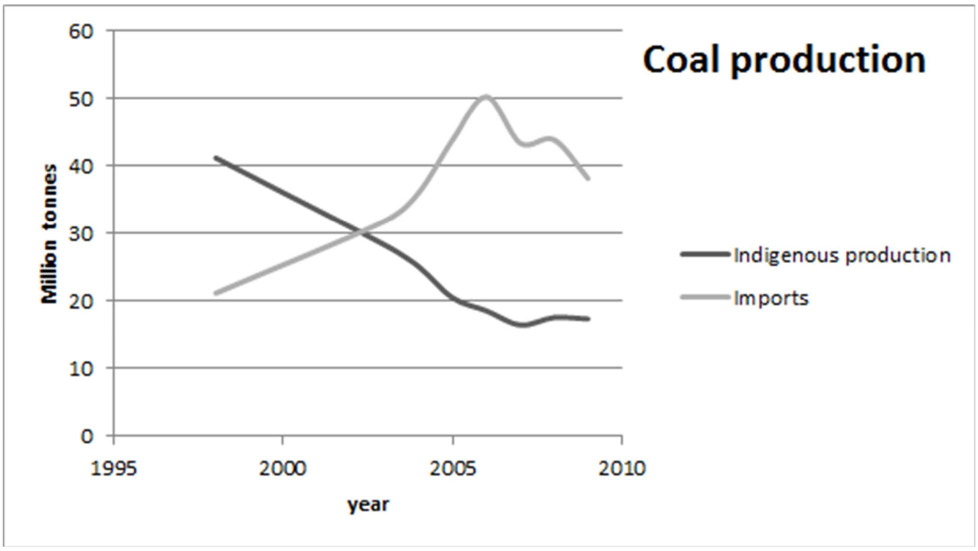

Figure 1.6: Coal production and import trend in UK [18]

The indigenous coal production also shows a decline as it is shown in Figure 1.6. Similar trends can be observed for the UK gas production which in 2005 was reaching more than 85 billion cubic metres per annum but it is expected to drop to about 20 billion cubic metres per annum in 2020 [18]

1.4 Gasification: History and today

During the 16th century in the UK laws were passed in order to restrict the use of forest trees to the glass and iron manufacturers and producers. An alternative fuel was required and this was coal. Until then, wood was used (cooked) in order to produce tar and pitch as a protection layer for the ships. The tar was mostly imported from the American colonies [19].

Archibald Cochrane has experimented and invented the process of destructive distillation using coal. Cochrane observed ignited gases in his lab after an accident that was caused by leaving the pressure to a kiln rise. He mentioned these ignited vapours to James Watt at about the same time (end of 18th century) when Watt hired a young person called William Murdock who came to Watt's factory in Birmingham in 1799 to discuss with him a process to produce gas. The Murdock's apparatus was a metallic container with coal inside and covered at the top, that was put on the fire to cook. The gases were escaping from a tube at the top of the container. Two gas burners were installed at the factory creating an odour that became known as the “Soho stink”. After that, gas lamps were installed in a cotton factory in Manchester [19].

Many examples of that time show the confidence that gas producers had in their “invention” such as Frederick Albert Winsor who renamed his company Gas Light and Coke Company in 1812 which made it possible to illuminate the major British cities using gas within six years. The implementation of the gas also had a social impact for example it made the streets during the night safer, increased the factory hours and thus increased the general production along with many other impacts [19].

In the 19th century, town gas that was produced from the gasification of coal, was used for heating and lighting. During the 20th century, fuels and chemicals were able to be produced using syngas. In 1902 Sabatier and Sanderens discovered the synthesis of hydrocarbons from the carbon monoxide hydrogenation by passing the syngas over Ni, Fe and Co catalysts. During the same period, the steam methane reforming producing hydrogen was commercialised. In 1910, the synthesis of ammonia was discovered by Haber and Bosch from hydrogen and nitrogen, known as the Haber process, and 3 years after the first commercial plant for ammonia production was commissioned. In 1923 Fischer and Tropsch managed to convert it into liquid hydrocarbons by passing syngas over iron catalysts. Many types of hydrocarbons have since been discovered [20].

The scarcity of fuels during the Second World War provided an opportunity to discover many new syngas conversion processes, especially in Germany where the gasification process flourished due to the need of an alternative fuel source. After the War, the rapid growth of the petroleum industry and the expensive, at the time, gas synthesis led to a decline in the syngas production. Many gas conversion processes were abandoned in order to be replaced by the oil processes. The few of them that continued to be produced using syngas was the production of methanol and ammonia.

One of the most successful Fischer-Tropsch processes in commercial scale, during the cold war, existed in South Africa where there was an abundance of coal reserves, and for political reasons the coal gasification had boomed [20].

The oil crisis in the 1970s further increased the scepticism over the oil dependence of many industrial countries and led to an increase of utilization of various synthesis processes. Over the years, the new regulations that were created for the safer and healthier use of coal also helped to increase the interest over the gasification and the synthesis processes. Since then, significant amounts of research and development have been held in order to optimise the gasification and synthesis process [20].

A number of gasification processes and technologies that were developed during the 1970s due to the oil crisis were abandoned and stopped during the 1980s due to the decline in the oil prices, making oil more commercially attractive. In the 1990s again there was an increase in interest in gasification and synthesis technologies due to the liberalization of the electricity markets that in its turn led to the requirement for cheap power production methods. Also, in the 1990s and in the first decade of 21st century the increasing need for renewables further enhanced the interest in gasification but by the year 2005 the commercial projects remained scarce [21].

While coal gas was mainly produced in entrained flow gasifiers, biomass had been gasified in small scale downdraft and updraft applications since late 1980s and beginning of 1990s. In recent years, downdraft process has become dominant due to the production of a lower amount of tars [21].

The use of biomass in the gasification process has grown over the last years but still, the largest thermal conversion method for biomass is combustion. Worldwide by the year 2000, the heat capacity of 200 GW_{th} was installed, using biomass, of which over 90% was based on combustion. Gasification applications, on the other hand, reached 1.4GWth in the same year [21].

In the 1980s gasifiers were installed for heating applications and were used in the paper industry and in cement kilns. In the 1990s the first Combined Heat and Power (CHP) application appeared as well as the Integrated Gasification Combined Cycle (IGCC) that promised higher efficiencies and lower costs. By 1998, syngas produced from biomass was co-fired with coal in certain power stations [21].

Lately there is a challenge to scale up gasification applications such as IGCC. Disadvantages of large plants are the high fuel transportation cost and the high initial investment cost [21] and thus higher efficiencies required in order to compensate for these disadvantages.

Nevertheless gasification technologies today are extremely promising and are of significant worldwide interest. In combination with the abundance of coal, the surplus of biomass wastes such as agricultural residues, and the highly volatile prices of oil, gasification can play a major role in the energy production market in the future.

2 Aims and objectives

Aims

The aim of this PhD is to attain optimisation of pelleting process by maximising the potential of pellets for them to deliver maximum energy production in thermal conversion processes with the minimum energy dissipation. Also, to connect the processes of pelletisation and gasification that might assist the standardization of pellets for industrial use.

Objectives

- To define the pelletisation parameters that affect the gasification process such as the feedstock moisture content, the feedstock particle size and the die diameter;

- To combine these parameters in the pelleting process and use oilseed rape straw (OSRS) to manufacture the pellets using these parameters;

- To determine the general quality of the pellets in terms of pellet density, bulk density and pellet durability;

- To utilise the OSRS pellets in order to produce gas and to examine the gasification performance of these pellets;

- To compare the performance of OSRS pellets with other types of biomass pellets and to identify the reasons of their differences;

3 Literature review

3.1 Biomass

3.1.1 Biomass types

Biomass means the biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste [22].

3.1.2 Lignocellulosic biomass and structure

Biomass is a part of a system that is controlled by energy flux and matter flux. The initial energy provider to the system is the Sun through the solar radiation that is captured in the process of photosynthesis by which plants capture light energy and transform it into the energy of chemical bonds in carbohydrates such as glucose and other organic compounds. Photosynthesis combines two common organic compounds, carbon dioxide (CO_2) and water (H_2O) to form glucose ($C_6H_{12}O_6$) with the release of oxygen. The stoichiometrical photosynthesis reaction is:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

The rate of photosynthesis in general varies in relation to light intensity, temperature and availability of water and nutrients [23].

Young living plant cells such as those found in leaves and young stems are mainly composed of cellulose (Figure 3.1) which is a long chain of glucose molecules which is contained within the primary cell wall.

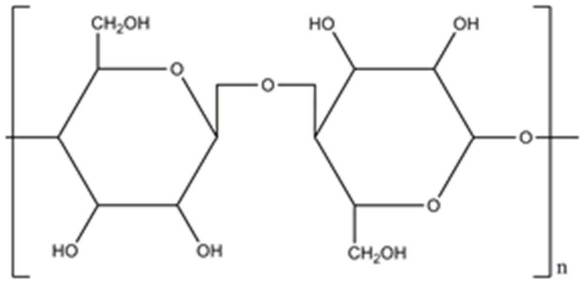

Figure 3.1: Cellulose fraction [24]

The secondary cell wall is found in mature cells that are no longer growing. Wood, for example, is mainly composed of lignin (Figure 3.2). Lignin is one of the most important structural compounds in nature [23]. Lignin wraps around cellulose, preventing biodegradation. Therefore combustion and/or gasification are suitable means of extracting the energy from lignocellulosic matter [25].

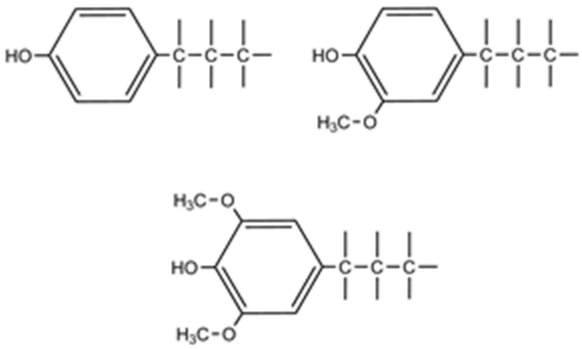

Figure 3.2: Some structural units of lignin [24]

3.1.3 Bioenergy

Biomass provides about 13% of world's energy requirements. The flux of dry matter of biological material in biosphere is nearly $250x10^9$ ty^{-1} incorporating around $100x10^9$ ty^{-1} of carbon. The energy bound in photosynthesis is $2x10^{21}$ Jy^{-1}. Of this, about 0.5% by weight is biomass as crops for human food [26]. This, therefore means, that only a small fraction of biomass is used for food while the rest could be used in a different manner.

In the developed world, however, the proportion of energy provided by biomass is much lower than 13%. In UK 4.6% of electricity comes from renewable energy sources with about the half of it provided by biomass. [27]. In the US, biomass provides 3% of the total energy consumption [28].

3.1.4 Agricultural residues, energy crops and wastes

The agricultural residues derived from food crops are the main research topic of this project. The two main bioenergy sources are the crops and the wastes. Crops involve normal wood for burning, plants for fermenting to ethanol and various other crops of which seeds are rich in oils and also crops that are solely used for energy production through combustion. Wastes involve wood residues, food crop wastes such as straw, animal wastes, municipal solid wastes, commercial and industrial wastes.

There is currently a huge environmental debate regarding the sustainable use of a forest, however the world's forests have been significantly reduced, causing environmental concern. A solution, especially for the energy sector, is the Short Rotation Coppice (SRC), which is coppicing fast growing trees and then harvesting them. The energy sector also utilizes agricultural crops which are non-woody energy crops such as Miscanthus, food crops with high capacity in energy such as sugarcane and maize and also crops that contain oily seeds like sunflower and oilseed rape [29].

On the other hand, wood and forestry residues such as those from wood industry, food crop residues like wheat straw or rice husks can all be considered as wastes. Wastes have the advantage that they are seen as "surplus" and thus can be used for energy production without interrupting the food production [29]. Therefore, the use of wastes helps to solve the problems providing more sustainable methods of dealing with waste and helping to meet the renewable energy targets.

3.1.5 Oilseed rape

Oilseed rape (OSR) is usually a tall, slightly bristly, biennial plant. Basal leaves are usually grey in colour, stalked and upper clasping the stem. The flowers of the plant are pale yellow in colour. Furthermore, the buds of the plant slightly overtop the open flowers. The plant is widely cultivated as it contains oil-rich seeds [30].

The seed typically contains 42% oil and the meal left after removing the oil is about 42% crude protein [31]. The oil is usually used in food but it can also be used in certain industrial processes as biofuel, lubricants, surfactants, surface coatings, polymers and also in pharmaceuticals [31, 32]. It is usually cultivated during two periods: the winter and the spring period. Winter is the commonest period of cultivation which results in high yields producing typically 3.7 t/ha of seed [31].

Advantages for growing oilseed rape straw are [33]:

- The ease with which the crop grows
- Suitability to a wide range of soil types
- Tolerance to weather variations
- Usefulness as a cleaning crop and good preparation for winter wheat

OSR is a “break-crop” meaning the fact that is a crop that helps to improve the yield of the following cereal crop, mainly wheat [34]. OSR straw quantities in UK are about 1.5 tonnes / hectare for about half a million hectares [35], while the seed production in UK, in 2009, was about 2 million tonnes [36]

The area used for oilseed rape is 581,000 hectares (Figure 3.3), yielding 3.4 tonnes/hectare, with total production of 1.95 million tonnes. For comparison, wheat occupies 1.8 million hectares yielding 7 tonnes/ hectare with a total production of 14.4 million tonnes (2009) [36]. This means that, the area occupied by OSR is just 3 times less than the area occupied by wheat (which is considered the most important arable crop). Another interesting fact is that, the entire area of UK is 24.4 million hectares, from which one can conclude that the area used for OSR production is 1/40 of the entire UK land [36]. The next two Figures (3.3 and 3.4) show the total arable land in UK and the land occupied by oilseed rape, wheat and barley, one can see the increase of oilseed rape over the years although the arable land itself has decreased.

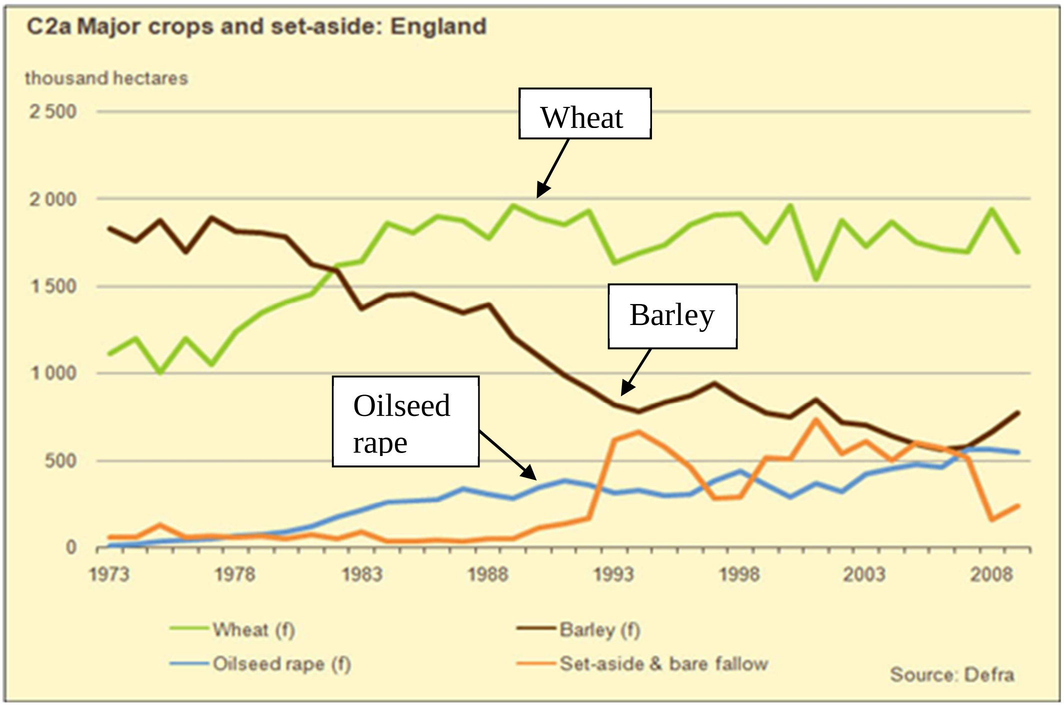

Figure 3.3: Major crops [37]

Source: http://www.defra.gov.uk/evidence/statistics/foodfarm/enviro/observatory/indicators/c/c2_data.htm

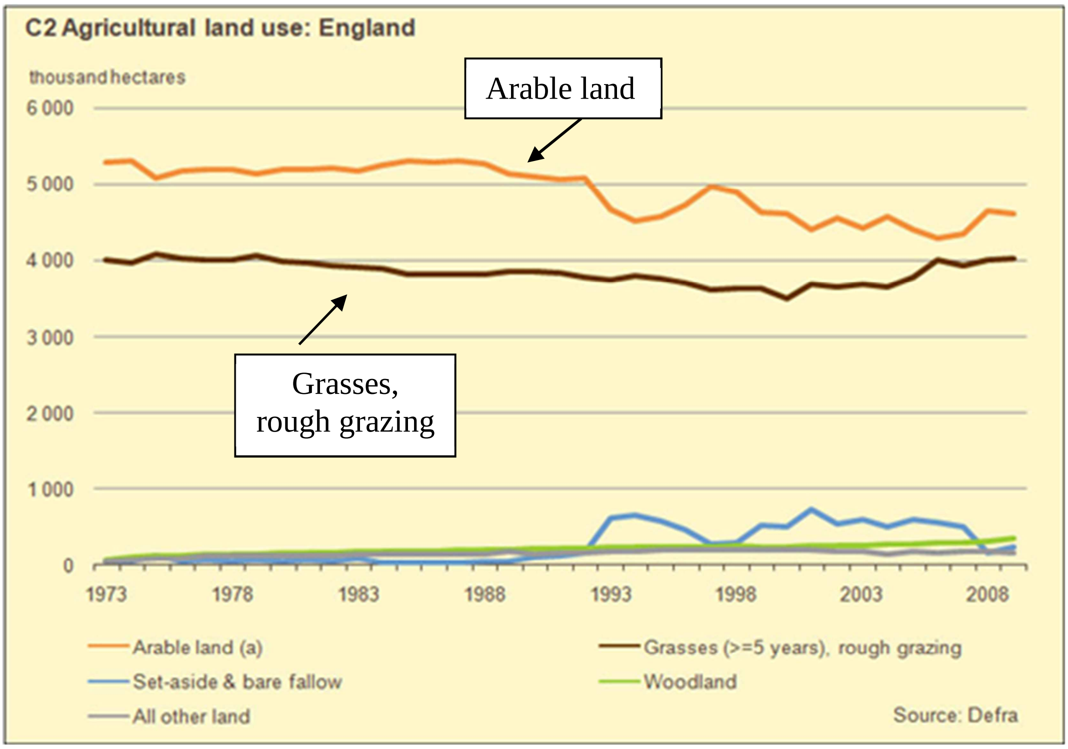

Figure 3.4: Agricultural land use [37]

Source: http://www.defra.gov.uk/evidence/statistics/foodfarm/enviro/observatory/indicators/c/c2_data.htm

3.1.6 Miscanthus

Miscanthus is a C_4 perennial crop that originally comes from Asia. It mainly consists of strong perennials and elongate-linear leaf blades and it is closely related to sugar cane [38]. In Europe it was first reported in Denmark in the 1935, imported under the name *Miscanthus x giganteus* [39]. Miscanthus was identified of having advantages that can constitute the plant an ideal energy crop [40]:

- High yield
- Perennial crop
- High photosynthetic conversion efficiency
- Efficient use of nitrogen and water
- Pest and disease resistant

Miscanthus is grown throughout the months of June and July. During the autumn and winter nutrients from the plant are sent back to the rhizome. Miscanthus is usually harvested during the winter or early the following spring. This pattern can be repeated for nearly 20 years which is the life time of the plant. In UK it is common to use Miscanthus for co-firing with coal in power plants [41].

3.1.7 DDGS

Dried distillers grains with solubles (DDGS) is the unfermented by-product of the ethanol production process [42]. The yield of the ethanol production process is about 370 litres of anhydrous ethanol per tonne of grains and 285 kg of DDGS [43]. As the most of the ethanol production plants function using natural gas, it was found that the DDGS with its high yield can be used to supply all or the required heat and electricity in the ethanol plant. DDGS is commonly used as feed for the cattle but it was found that it contains a certain form of fat that some species cannot tolerate [44].

3.2 Pelletisation and pellet properties

Biomass and, in this case, lignocelluloses can be utilized and transformed into solid, liquid and gaseous fuels through various physical, chemical and biological conversion processes.

3.2.1 Overview of pelletisation process

Biomass is generally difficult to handle, usually non-uniform and with a low energy density, therefore pelletisation appears desirable to allow easier and more economic storage, transportation and energy conversion characteristics [45]. Pelletisation is a method of increasing the bulk density of biomass by applying mechanical pressure [46]. This method can give multiple advantages in biomass; amount of dust is decreased, energy density is increased and fuel becomes uniform and thus allows easier and more efficient control during combustion and gasification [47]. For example, bulk density of loose straw is approximately 40 kg m^{-3}. Pelletisation of straw would increase the bulk density to nearly 600 kg m^{-3} which would make straw easier to handle, transport (Table 3.1) and feed into a combustion or gasification unit [46].

Table 3.1: Forms of straw packing [48]

	Chopped straw	High pressure bales	Big bales	Pellets
Specific weight in kg/m^3	50	80 - 100	100	300 - 500
Storage space in m^3/60x10^3 kWh	370	200	245	41

3.2.2 Pelletisation methods – types of pelleting units

Pelletisation process consists of certain sub-processes such as grinding, drying, milling and pelleting (Figure 3.5). The properties of these sub-processes are defined in terms of the end use of the pellets. Initially, the pelletisation process was developed for the livestock feed industry but the utilization of pellets also expanded into the thermal conversion systems such as gasification or combustion.

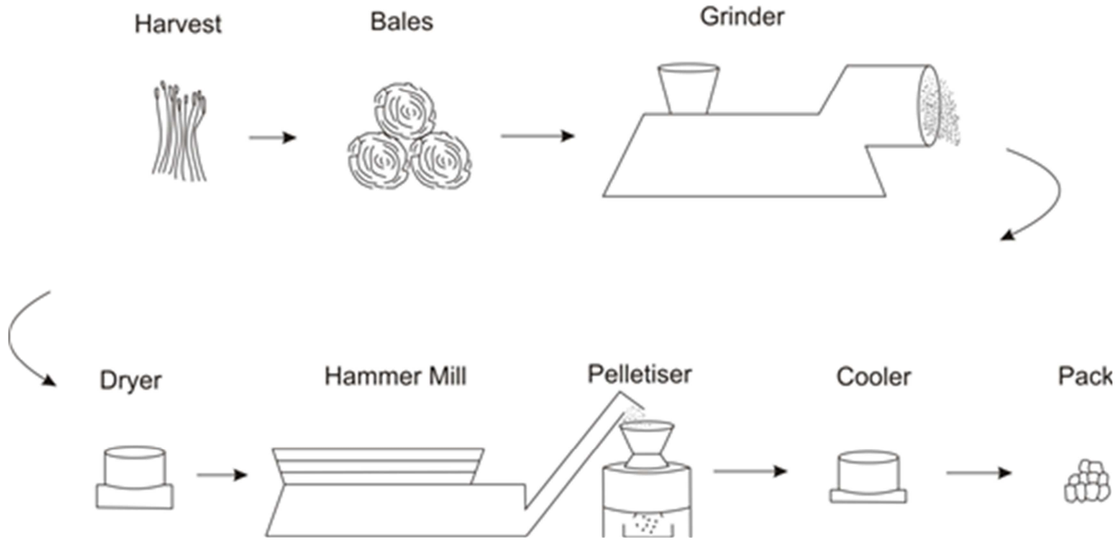

Figure 3.5: Pellet process

Physical and chemical characteristics of feedstock determine to some extent, the process of pelletisation. Wood chips, shavings and sawdust, which all can be considered wooden materials, are slightly different in these properties from herbaceous biomass and agricultural residues such as oil seed rape straw or wheat straw. Because of that, the pelleting process properties are also slightly different [49]. Material's moisture content, particle size, density, fibre strength, lubricating characteristics and natural binders, have already been found that affect the process of pelletisation [47].

3.2.3 Pre-treatment

Few of the properties mentioned above can be controlled or can be affected by the feedstock pre-treatment. In the pelletisation process, pre-treatment mainly consists of two different processes; drying and grinding.

Drying is usually required to decrease the moisture content of biomass which in many cases exceeds an appropriate value for pelletisation (between around 6-18% moisture content).

Milling is also required in order to transform the feedstock into a more uniform material. The material after milling process consists of particles which are of equal size and similar moisture content. This homogeneity makes the pellets more durable [49]. Furthermore, milling brings size reduction which in turn leads to an increase in particle surface area facilitating inter-particle bonding [50]. In general the purpose of pre-treatment is to alter the feedstock in a fluidic manner where a low friction coefficient is created between the internal die surface and the fibre [47].

3.2.4 Pelleting and post-pelleting

Pelleting process is typically carried out in a conventional pelletiser. Loose biomass feedstock is fed into the pelletiser where the presence of a die and the pressure of the rollers upon the feedstock force it to pass through the die and form pellets. Pelletisers are usually equipped with knives (or blades) which cut the pellets to the desired length. There are two types of conventional pelletisers; flat die and ring die type. In flat die pelletiser, the die remains stationary while rollers rotate and compress the feedstock, while in the ring die pelletiser, is the die itself that rotates [49]. In any case, when the material passes through the die holes, friction causes the die to heat up and the temperature increases to around 75 – 85 ^{o}C. Then, lignin inside the material, starts flowing off the fibre; Lignin in this state has the ability to bind the fibres [47]. Pelleting process results in constructing a uniform fuel with many times higher bulk density compared to the loose material [47], and so is attractive to operators of biomass and energy processes.

Cooling is considered a very important part in the pelletisation process. The typical pellet temperature after leaving the pelletiser is around 80-90 ^{o}C. Cooling of the pellets makes them hardening due to lignin stabilization especially on the surface of the pellets [49]. The general binding mechanism is described in section 3.2.5.

3.2.5 Binding mechanism

While pressure is not yet applied and particles are in a close distance between them and in a confined space, they start to rearrange and thus form a mass. At that point the feedstock particle properties are still retained even though that energy has already been dissipated due to interparticle and wall-particle friction. When high pressures are applied, particles are compacted even further subsequently forcing them to undergo elastic and plastic deformation and thus the area of contact between the particles is increased [50]. Plasticity of particles can be also affected by the temperature and moisture content. High moisture content leads to an increase of the interparticle space and thus more compression energy is dissipated. On the contrary, low moisture content increases the friction during the process affecting the plasticity [51]. Theoretically the reduction in volume continues until the pellet density approaches the density of the particle.

In order to further investigate the binding mechanism, forces between the particles and various binding phenomena should be also mentioned, such as Van der Waal forces, solid bridges, capillary pressure, or mechanical interlocking. Electrostatic, magnetic and Van der Waal forces are the cause of an attraction force between the particles which depends on the particle size and the interparticle distance. In addition, the presence of a liquid such as water enhances the binding of the particles due to the capillary pressure and the interfacial forces [52].

Interfacial forces are in general connected with the individual movement of small, in this case, solid particles in the bulk of a phase [53].

During the binding process interlocking of the fibres also takes place when, due to the pressure, the particles are wrapped and overlap each other; a process which also assists the binding process [52].

The binding mechanism is also enhanced by lignin. The addition of heat in biomass forces the lignin to become softer initially and to exhibit thermosetting properties due to irreversible cross-linking and curing. It was observed by van Dam *et al* [54] that at the temperature of around 140^{o}C, lignin shows an exotherm which basically denotes the irreversible cross-linking of the lignin polymer. That is the reason why pre-treatment should always be performed below that temperature.

3.2.6 Effect of pelleting properties on the quality of pellets

White [55] showed a linear correlation between the Higher Heating Value (HHV) and lignin content of wood (extractive-free). As the lignin content increases the heating value also increases. It was also observed that pellets had lower heating value and higher ash content compared to the feedstock because of the loss of volatiles during the drying process [56].

There are many other reports that investigate on the effect of fuel characteristics or pelletisation properties to the pellet quality. Kaliyan *et al* [57] reviewed the pellet durability. Durability is the abrasive resistance of the pellets; adding fats or oils into the feedstock, reduces the durability of the pellets. Fats and oils act as lubricants between particles and between the particles and the die wall. Thus, friction is reduced and pressure is decreased resulting in lower pellet durability. The quality of pellets could be increased by adding starch and protein which could act as a binder. Briggs *et al* [58], managed to increase the pellet quality by increasing the protein content. Alternatively an increase in oil causes a decrease in pellet quality; the upper oil limit was found to be 5.6% with a protein content of 20% [58]. Durability of pellets can decrease if not cooled down; stresses appear between the inner (warm) and the outer (cold) part of the pellet that can cause cracks [57]. Experiments and modelling procedure in reed canary grass showed that moisture content was the most influential factor for bulk density and durability responses [59].

Durability also depends on the feedstock particle size. The smaller the particle size is, the greater the durability. Small particles are more susceptible in moisture compared to large particles. Large particle on the other hand are more susceptible in cracks and that causes fracture of pellets [57]. Furthermore a study by Bridgeman *et al* [60] showed that the size reduction process of biomass is not done in a uniform manner and instead, it was observed partial separation between organic and inorganic matter in different size particles; larger particles have higher carbon and volatile content that leads essentially to increased heating value. A study by Lehtikangas [56] confirmed the correlation between durability of pellets and lignin content and furthermore showed that moisture had also a positive effect.

Moisture can act as a lubricant and as binder. Moisture increases the contact area of the particles and enhances the development of van der Waals forces by H-bonding. Many other studies showed that increasing moisture content up to point helps to increase pellet durability [57]. A study by Sokhansanj [61] showed a correlation between bulk density and moisture content. Bulk density correlates with moisture content; at low moisture content grinded alfalfa particles weighted less and at high moisture content the particles increased their volume due to swelling [61]. Finally, a correlation was found between moisture content and density. As moisture content increases, density decreases exponentially because the volume was increased during sorption of moisture [61].

Other studies showed that the larger the die length-to-diameter ratio is, the higher the durability is. A decrease of die diameter up to a point can cause an increase in the shear applied to feedstock affecting positively the durability of the pellet [57]. In addition, it was found that the pellet length had no influence on bulk density but pellet density had a positive effect on bulk density [56].

However, a study by Obernberger [62] didn't observe a correlation between abrasion (durability) and particle density as well as a correlation between abrasion and moisture content. An explanation was that pellets were manufactured in different plants, using different pellet equipment; an indication that abrasion may also depend on many different parameters.

It can be seen from all the above that the pelleting parameters could play an important role on the pelleting process and the pellet quality. Some of the parameters and their effect in the pelletisation process derived from the literature above can be seen in the Table 3.2.

Table 3.2: Parameters and their effect in pelletisation process according to literature

Parameter	**Effect**	**Reference**
Lignin	Act as binder. Linear correlation with heating value.	[56] [55]
Fats/oil – Starch/protein	Oil act as lubricant. Oil reduces durability. Increased oil reduces quality Starch/protein act as binder – increased pellet quality	[57] [57] [58] [58]
Moisture	Act as lubricant and as binder. Durability – increases pellet durability by adding moisture up to a point. Bulk density – increasing moisture, bulk density increases to a point and then decreases. Density – increasing moisture, decreases particle density.	[57] [57] [61] [61]
Particle size	Durability – the smaller the particle size the greater the durability. Larger particles-higher % of C and volatile-increased heating value	[57] [60]
Die diameter	Durability	[57]
Pellets density	Bulk density – positive effect	[56]

The energy required to manufacture pellets plays an important role in the energy balance of the whole process. Sokhansanj [63] states that pelleting process requires more than 60% of the total energy used in pelleting to overcome friction. This study also observed that increasing the temperature of the pellet dies, density and durability of pellets increase and at the same time energy consumption is decreased.

A review by Chen *et al* [49] for the Supergen Bioenergy project (2008) states that straw as a fibrous material and with low lignin content will require high energy input (near 50 kWh/t) to be pelletised compared to other non- fibrous material such as sawdust.

Regarding the economics, in general a small scale pellet plant would be more expensive to operate and that leads to an increase in pellet price due to the scaling economics, cost of personnel etc. Cheap pellets could be produced from a plant with capabilities of 10 t/h or more [64]. The major cost factors in the pelleting process are the raw material and the personnel while the dryer and pellet mill costs follow [64].

3.3 Thermal conversion processes

The thermal conversion of biomass requires consideration; the purpose of thermal conversion varies. Thermal conversion can be used for heat and/or electricity generation and for the production of synthetic fuels and chemicals.

The three main methods of thermal conversion are:

- Combustion
- Pyrolysis
- Gasification

Pyrolysis is not going to be explored separately as a part of this review; however it will be mentioned as a part of other processes.

3.3.1 Combustion

Combustion of a fuel is simply the process of burning the fuel in the presence of oxygen. Combustion in general is a self-sustaining reaction of a fuel and an oxidant such as a hydrocarbon and oxygen that produces carbon dioxide, water and energy. Combustion of biomass can be expresses as the combustion of cellulose in the following reaction [24]:

$$(C_6H_{10}O_5)_n + 6nO_2 \rightarrow 6nCO_2 + 5nH_2O$$

Combustion process can be divided into four different stages [65]:

1. Heating and drying
2. Devolatilization (or pyrolysis)
3. Volatile combustion
4. Char combustion

Heating and drying

The process starts by the increasing heat that dries out the biomass so that the contained moisture is released in the form of steam. Here, particle size of the fuel can affect the heating rate [66].

Devolatilisation

Devolatilisation, or pyrolysis, is the thermal decomposition of biomass into a range of gaseous species, tar and char. Thermal decomposition of biomass starts at around 150 to 200^{o}C at the surface of the fuel particle and results in the evolution of various volatile organic compounds [24]. Devolatilisation can be affected by various factors such as the rate of heating, the particle size, the type of the fuel and the pressure [66]. Devolatilisation products can be separated into three categories [67]:

- Light gases such as CO_2, CO, H_2, H_2O, CH_4,
- Tars which are mainly heavy organic and inorganic molecules in the form of gases or liquids
- Char which is the solid residue that remains

Using Thermo-Gravimetric techniques, Raveendran *et al* [68], visualized and recorded the following devolatilization zones for the lignocellulosic material [68]:

Zone 1 [<100^{o}C]: Mainly moisture evolution

Zone 2 [100-250^{o}C]: Decomposition of extractives

Zone 3 [250-350^{o}C]: Mainly hemicellulose decomposition

Zone 4 [350-500^{o}C]: Mainly cellulose and lignin decomposition

Zone 5 [>500^{o}C]: Mainly lignin decomposition

Volatile combustion

In general, it is difficult to separate the devolatilisation and the combustion of the volatiles because the two processes overlap. The volatiles, combust in a diffusion flame at the interface between the unburned volatiles and the oxygen [66]. In more details, a diffusion flame develops around the fuel particle, while the position of the flame front depends on the oxygen diffusion rate to the flame and on the volatile release rate [66]. The lower oxygen diffusion rate we have, the further the flame front is from the particle surface. Due to the fast burning of volatiles, their combustion rate is usually defined by their release rate [66].

Char combustion

The remaining part of the fuel after devolatilisation is the char. Char burns relatively slow and its combustion starts after the combustion of the volatiles even though the two processes often also overlap. In order for the char particle to combust, oxygen from the bulk stream has to reach the surface of the particle. Once the oxygen reaches the surface, it undergoes an oxidation reaction with the carbon on the surface and CO and CO_2 are produced [66]. As the char is porous, oxygen under favourable conditions, diffuses into them and oxidizes the carbon at the inner part of the char [66].

3.3.2 Gasification

Gasification is considered to be the conversion of carbonaceous fuels into a combustible gas. The gas consists of 6 major species and a number of minor species. The major species are: CO, CO_2, H_2, H_2O, CH_4 and N_2. The gasification process is initiated when combustion products such as CO_2 and H_2O, in a low oxygen environment with elevated temperatures, are reacting with char (it can be assumed that it is pure carbon) where it forms syngas (CO + H_2). By definition, therefore, gasification requires partial combustion to take place in order to form combustion products and also to increase the temperature in the reactor.

During the partial combustion and devolatilisation (or flaming pyrolysis [69]), the material is heated in a low oxygen environment and pyrolysis products (such as CO and H_2) are produced along with combustion products. The char produced during flaming pyrolysis (FP) and the higher temperatures in the reactor enact a series of endothermic reactions that causes the production of more CO and H_2 and also considerable amounts of methane [69, 70]. The partial or complete oxidation reactions are [71]:

$C + ½ O_2 \rightarrow CO$	-111 MJ/kmol	(a)
$CO + ½ O_2 \rightarrow CO_2$	-283 MJ/kmol	(b)
$H_2 + ½ O_2 \rightarrow H_2O$	-242 MJ/kmol	(c)

The combustion or partial combustion products are then reduced in a complex process involving char, high temperatures and gases:

$C + CO_2 \rightarrow 2CO$	+172 MJ/kmol	(Boudouard reaction)	(d)
$C + H_2O \rightarrow CO + H_2$	+131 MJ/kmol	(water gas reaction)	(e)
$C + 2H_2 \rightarrow CH_4$	-75 MJ/kmol	(methanation reaction)	(f)

As someone might observe, all the three last reactions, are heterogeneous, but during the reduction of the material also complex homogeneous reactions occur:

$CO + H_2O \rightarrow CO_2 + H_2$	-41 MJ/kmol	(water gas shift reaction)	(g)
$CH_4 + H_2O \rightarrow CO + 3H_2$	+206 MJ/kmol	(steam methane reforming reaction)	(h)

3.3.3 Gasification systems

Gasification systems can be split into three distinct categories: updraft, downdraft and fluidised bed gasifier. In an updraft system, biomass is fed at the top of the gasifier and air at the bottom. The gas leaves the gasifier from the top and the ash from the bottom (Figure 3.6). Advantages of the system are: the simplicity, high heat exchange capabilities, which lead to high gasification efficiency and a low temperature of the gas at the exit. Furthermore, fuel with high moisture content can be used (dry zone is at the top so fuel dries quickly) and also high char burning rate was observed. A disadvantage is the high quantity of tars and pyrolysis gases (heavy hydrocarbons) due to the fact that they do not pass through the combustion zone [65].

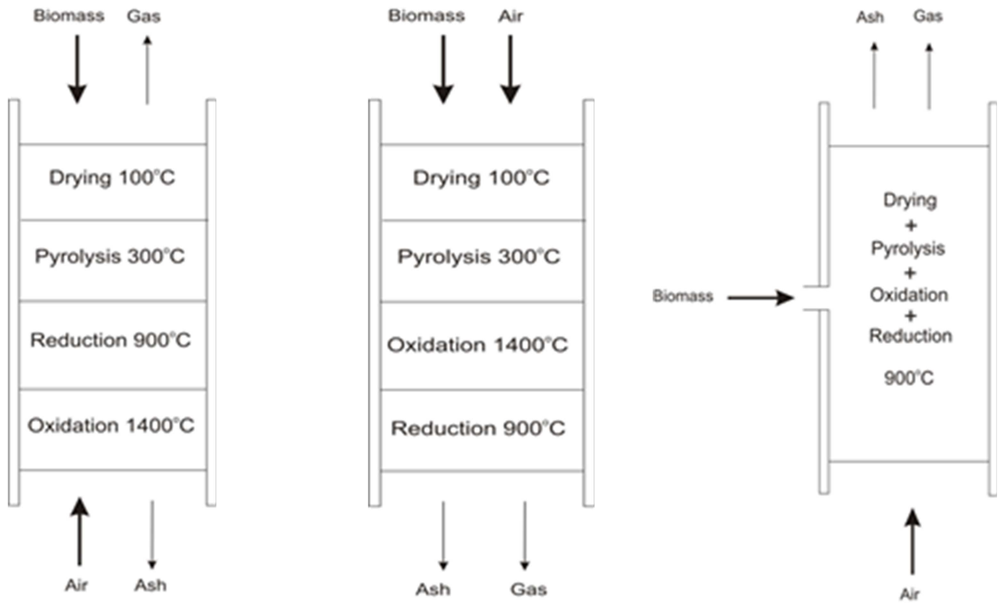

Figure 3.6: Updraft, downdraft and fluidised bed gasification system [50]

In a downdraft system, biomass is fed at the top and air can be also fed at the top or at the sides of the gasifier. Gas and ash are leaving the gasifier at the bottom. Advantages of the system are: the relatively reduced quantity of tars at the end and the high conversion of pyrolysis products. Disadvantages are: the large quantity of ash and dust particles because gas has to pass through the combustion zone where particles are collected along with it; there is no flexibility in terms of fuel use (4-20cm in size and less than 25% of moisture content). Furthermore, the efficiency of the system is low because of the high temperature of the gas at the exit [65].

In a fluidised bed system, biomass is fed into a suspended bubbling fluidised bed. Air enters at the bottom of the system and the gas leaves at the top. In the bed, biomass is mixed with the sand quickly resulting in fast pyrolysis. Advantages of the system are: high heat exchange capabilities and high reaction rates due to the intense mix at the bed, flexibility in fuel use and low melting points because of low gasification temperature (750 – 900^{o}C in fluidised bed and 1200^{o}C in fixed beds). Disadvantages are: high quantities of tars and dust particles in the gas stream, high gas temperatures (alkali metals remain in vapour state), complex operation due to the need of continuous control of fuel and air [65].

Spouted bed is another category of gasifiers. Spouted beds are only different from fluidised beds in the dynamic behaviour of the solid particles. The spouted fluidised bed, being a combination of the two, is in general similar to the fluidised bed [72].

3.3.4 General effects of reactor and process parameters

The gasification of char is a much slower process compared to the pyrolysis of char and thus the char gasification plays a major role in the overall process efficiency [73].

Pressure

Pressure usually has a positive effect on the side of the reaction which it occupies the least amount of space, and thus the side of the reaction with the least number of moles. For example, the right hand side of the methanation reaction is positively affected by an increase in the pressure and thus it can be observed an increase of CH_4 concentration in the syngas. On the other hand, reactions such as the water gas shift reaction are not affected by pressure alterations because there is no volume change [74]. Furthermore, a model developed by Higman *et al* [71] shows that a pressure increase, results in the decrease of CO and H_2 and the increase of CH_4, CO_2 and H_2O. The model also shows that the gas heating value increases due to the extra CH_4 produced. According to the Ullmann's Encyclopedia of Industrial Chemistry [75], the Boudouard reaction and the water gas reaction products show a decrease with an increasing pressure. On the other hand, the methanation reaction products are increased with an increasing pressure.

Temperature

In general terms, an increase in the temperature, increases the rate of the reactions. In the range of low temperatures (about 1-700^{o}C), the rate controlling step is the rate of the chemical reaction (kinetic rate). In the range of mid temperatures (700-1000^{o}C) the chemical reaction rate is still high but is limited by the pore diffusion. Finally in the range of high temperatures (>1000^{o}C) the overall rate is controlled by the surface diffusion rate [71, 74].

In general, high temperatures favour the products of the endothermic reactions [75], whereas high temperatures may have adverse effects. A high temperature may be responsible for the melting or softening of the ash and this can cause the process to stop in fluid-bed and moving bed gasifiers [71]. Furthermore, an increase at very high temperatures, increases the oxygen consumption, reduces the number of active sites during the pyrolysis above 1000^{o}C and generally reduces the overall process efficiency [71, 74]. According to a model by Higman *et al* [71], an increase in temperature results in an increase of the concentration of CO and a decrease in the concentrations of CO_2, CH_4 and H_2O, whilst the concentration of H_2 stays fairly constant. The model also shows an increase in the O_2 demand in the process. According to Ullmann's Encyclopedia of Industrial Chemistry [75] the Boudouard reaction and the water gas reaction products are favoured by an increase of the temperature in constant pressure. However, the methanation reaction products are decreased with an increasing temperature.

Other process control properties

The equivalence ratio (ER) is a very important parameter in the gasification process and describes the ratio of the actual air that was used in the process over the stoichiometric (theoretical) air. Generally speaking, if the ratio is 0.8<ER<1.2 or more, then the process is combustion and if it is ER<0.5-0.6 the process can be described as gasification. Usually with a very low ER (<0.25) the char is not fully converted, the production of tar is increased and the gas heating value is decreased. An increased ER (above 0.4) results in excess complete combustion products that also lead to a decreased gas heating value. Thus, the highest conversion efficiencies lie in between [74]. Furthermore the bed temperature increases with an increasing equivalence ratio due to the higher supply of oxygen and the consequent combustion that takes place [74].

The gasifying agent has a major role in the gasification process. In air blown gasifiers, the Boudouard reaction is the dominant one and typically CO is higher than the H_2. On the other hand, in steam blown gasifiers the water-gas reaction becomes the dominant and thus a high amount of H_2 is observed in the syngas [74].

3.3.5 Thermal conversion of biomass and biomass pellets

In gasification processes, the composition of the resulting gas depends on: the properties of biomass, the gasifying agent and the process conditions. One of the main properties of biomass that affect the composition of the gas is the moisture content. The higher the moisture content, the more gasifying agent is needed in order to evaporate this moisture. Gas that is produced from high moisture content biomass contains higher quantities of H_2O, H_2 and N_2 compared to gas produced from dryer biomass. In addition, if the gasifying agent is air then the gas may contain up to 60% vol N_2 [70].

Biomass ash content plays a role on the conversion, and also higher ash content leads to lower net overall conversion efficiency [76]. Ash and carbon content affect heating value, an increase of 1% ash leads to a decrease of 0.2 MJ/kg, and an increase of 1% carbon yields an increase in the heating value by 0.39 MJ/kg [77].

The size of pellet affects gasification rate, but very little the pyrolysis rate [78]. Generally, the larger the pellet is, the slower the gasification, whereas, the smaller the pellet, the smaller the relative volume decrease of char [78]. This is likely to be due to the differences, of the small and large pellets, in bed porosity and species pore-diffusion. Particle size also affects the heat transfer rates in combustion: small particles burn faster than large particles [77]. A study, using a fluidised bed combustor showed that high-density and small-size biomass particles favour combustion [79]. The smaller the fuel size the better the mixing in the bed. The same study indicates that burning rate depends on particle porosity; the higher the particle porosity, the higher the burning rate is [79].

An advantage of biomass is the high reactivity of fuel and char, which is in fact, higher than coal. This is due to the volatile content which is usually two or three times higher than in coals. In addition there is an increase of total gas yield with increasing temperature [80, 45].

As mentioned before, tar formation constitutes a significant problem in gasification. Previous experiments in fluid bed steam gasification using calcined limestone as a bed demonstrated that an increase in gasification temperature from 650 to 750^{o}C results in a 23-29% increase in low heating value (LHV) and a 5.5-13% decrease in tar yield [81].

There are other disadvantages which are worth considering with regards to agricultural residues in combustion and gasification processes. These residues contain alkali metals such as potassium and sodium that may react, during combustion, with the silica to form alkali silicates. This leads to the formation of ash with a low melting point and in turn causes sintering and slugging problems. Alkalis can also react with sulphur to give alkali sulphates on the heat transfer surfaces [77]. On the other hand, Di Blasi [73] states that alkali metals can act as catalysts in gasification and combustion heterogeneous reactions speculating that char reactivity is much more depended on the amount and composition of the ash rather than the nature of the fuel [73].

Biomass ash can act as a catalyst for gasification reactions such as the water gas shift reaction [82, 83]. On the other hand, in a downdraft gasifier, high amounts of ash can inhibit the downdraft flow of the gas. In addition, the ash may sinter and fuse. The sintering of the ash as well as the melting point of the ash are mainly depended on the temperature. Tamman and Huttig temperatures could indicate at which temperature the sintering will occur [84]. Nevertheless, Miles *et al* [85], pointed out that solely the investigation of the ash fusion temperature cannot predict the behaviour of ash deposits and how this may affect the whole process. Therefore, it is also important to investigate the behaviour of combination of minerals inside the reactors themselves. Biomass contains high amounts of alkalis and other elements and the combination of these minerals can cause different behaviours in the gasification processes. For example, Baxter *et al* [86] reported that the melting point of silica based deposits decrease from 1700^{o}C to 750^{o}C as potassium is introduced to form potassium silicates. The introduction of additional alkalis or alkaline earth materials could lower the melting point even further. Similar results can be found in the literature by other authors too; Monti *et al* [87] indicated that ratios between K, Ca and Si should be taken into account to assess the biomass fuel quality and also that biomass fuels containing high amounts of Ca and Si, along with low amounts of K are better suited for conversion processes. Beck *et al* [88] reported the reduction of gaseous phosphorous compounds with increasing amounts of Ca. Finally Steenari *et al* [89] showed that material with high sintering temperature did not contain any KCl or K_2SO_4 and also showed that the material with low melting point contained both the salts along with phosphates with a high K/Ca ratio.

Other parameters also affect the gasification process. Reactivity of char is also depended on temperature and residence time in the reactor. An increase in temperature and residence time brings a decrease of the gasification and combustion reactivity of char [73]. In addition, a study by Rhen *et al* [90] states that char combustion time is positively correlated with pellet density. In addition the author speculates that the type of raw material might have greater influence than the pellet density [90].

Regarding cost and energy efficiencies, Bridgwater [91] stated that the potential for biomass relies only in the processing of low-cost wastes, however the author didn’t consider the potential of pellet manufacturing [91]. A study by Faaij *et al* [76] aimed to reveal efficiencies and costs of equipment that are most appropriate for electricity production and proposes a system with high efficiency over a range of biomass material. Fuel is not pelletised however, so no deductions can be made.

3.4 Downdraft fixed bed gasification process

In the downdraft gasification process, the fuel is fed from the top and the gasifying agent (air, steam or carbon dioxide) is fed either from the top or the sides of the gasifier and travel downwards and thus the name downdraft. The bed of the gasifier in steady state conditions forms four distinctive layers; from the top: drying zone, devolatilisation or flaming pyrolysis zone, combustion or oxidation zone and finally the reduction or gasification zone at the bottom of the reactor. Furthermore below the reduction zone there is a layer of ash as a result of the reactions that occur at the four distinctive layers above it [74].

In the first top zone the biomass is heated up and thus it is getting dried. The first zone also acts as a heat insulator. Below the drying zone is the flaming pyrolysis zone which it receives its heat through the third zone, which is combustion, by conduction and radiation. A small amount of air is used by the flaming pyrolysis zone which burns in a fuel-rich flame. The flaming pyrolysis zone creates mostly the tars and vapours and the char in the process which they burn in the third zone, the oxidation zone, generating heat for the pyrolysis and the following reduction or gasification reactions and also generating pyrolyzed char and ash and very hot gases containing carbon dioxide and steam. These gases react and reduced into carbon monoxide and hydrogen as they pass over the char, forming the fourth zone, the reduction or gasification zone. Due to the endothermic nature of the reactions the temperature falls in comparison to the temperature exhibited by the combustion zone. Following the endothermic reactions a layer of hot ash and unreacted char is formed at the bottom of the reactor. In this layer a part of the unconverted tars is cracked and thus making the downdraft gasification, the process with the lowest tar content in the gas stream in comparison to other types of gasifiers [74].

3.5 Spouted fluidised bed gasification process

The spouted fluidised bed is a type of fluidising bed, which is used for fluidisation of coarser particles compared to the common fluidising bed. There is a fluid (air in this case) that is injected through a single inlet at the centre bottom part of the bed. If the velocity of the air is high a hollow central core stream of particles rises rapidly in the bed until it breaks the surface of the bed. A fountain is then created on the surface of the bed that carries the particles to the periphery of the bed around the central spout (see Figure 3.7). The particles at the periphery of the bed (or annulus of the bed) travel slowly downwards and in some extent, inwards. When the particles traveling downwards meet the central spout, once again they are injected upwards forming the fountain and back to the annulus to complete the cycle. This cyclic pattern proved to have a great advantage in the controllability of coarse particles [92].

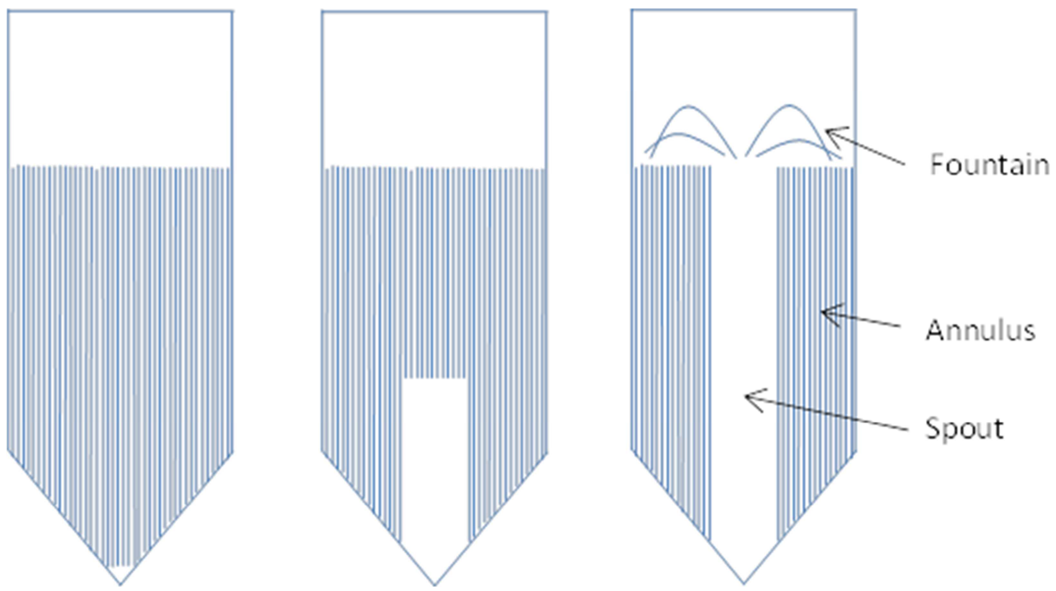

Figure 3.7: The formation of the spouted fluidised bed

With the exception of the particle size (spout bed has advantage using coarser particles over the fluidising bed) and the geometry of the column, there are several other differences between the two types of beds such as: 1) there is uniformity of temperature in a fluidising bed but not in the spouted fluidising bed, 2) the axial gradient of pressure is independent of bed height in the case fluidising bed but not in the case of spouted fluidising bed, 3) there is a less ordered and more complex gas and particle motion in fluidising bed but, on the other hand, more orderly in spouted fluidised bed, 4) there is a broad range of bed depths and superficial velocities in fluidising bed but a limited range in the spouted fluidising bed [93].

There are other important differences between fluidising and spouted fluidised bed. The pressure drop in the fluidising bed becomes steady when the minimum fluidisation velocity is achieved [92]. On the other hand, the overall pressure drop of the spouted fluidising bed is reaching a peak and then decreasing after the minimum spouting velocity is achieved [92]. In addition, the minimum fluidising velocity is independent of the depth of the bed but the minimum spouting velocity depends on the depth of the bed [92]. If the gas velocity is increased above the spouting velocity, which corresponds to the maximum bed depth, then either slugging or low quality fluidisation is observed [94]. Also, a great advantage of the spout bed, apart the efficient gas-solid contact, is the excellent solid-solid contact due to the vigorous agitation of the bed [92].

Initially the spouted bed technology was used in order to dry suspended particles and other solutions [95]. However in the early 1980s, the first publications appear for spouting bed gasification using mainly coal as a fuel. Since then, the spouting fluidising gasification technique has been developed and studied for coal gasification; however, the biomass spout bed gasification was not studied thoroughly.

3.6 Chapter summary

As has been discussed in this chapter, further research is required to fully understand the biomass and more specifically, the biomass pellet gasification in a spouted fluidising bed as well as in a downdraft gasification process. Due to the fact that pellets that were manufactured using oilseed rape straw haven't been used thoroughly in research and due to the fact that oilseed rape is an important plant in British agriculture, it is clearly an excellent candidate for this purpose.

The physical and chemical characteristics of the pellets dictate the gasification process. The physical characteristics of the pellets and the pellet quality are highly affected by the pelleting process. Thus, it is important to connect the two processes of pelletisation and gasification since no research study, to the author's knowledge, has investigated the effect of the initial pelleting parameters on the gasification process, this would therefore be the main subject of this project.

In addition to this the pelleting parameters have an enormous effect on the pelleting process, which is not discussed elsewhere in the literature; the parameters may correlate with the pellet quality, which is not discussed thoroughly in the literature. Finally, the chemical characteristics of oilseed rape straw pellets require thorough investigation, since there is a gap in the knowledge, which could be accomplished by comparing them with other biomass pellets.

4 Experimental procedure

4.1 Pelleting parameters

The aim of this thesis as outline in Chapter 2 is to study the effect of various pelleting parameters in the gasification process. The experimental procedure is composed of a series of tests of pellets gasification. The main part of the procedure is the gasification of oilseed rape straw pellets and the effect of pelleting manufacturing properties in the gasification process. Additionally the comparison of the OSR straw pellets with E-On Miscanthus pellets and dried distillers grains with solubles (DDGS) is explored.

Three different pelleting properties are defining the spectrum of the oilseed rape straw pellet experiments. The properties were: the feedstock moisture content, the particle size (or the screen size) and the die diameter. The properties and their variations are shown in Table 4.1. Eight different pellet variations were produced out of the combination of properties mentioned before and these pellets are tested in two different pilot scale gasification units in order to investigate on the viability of these pellets in terms of the output gas quality and process stability.

Pelleting process is characterised by altering three different properties at their lowest and highest possible values.

Table 4.1: The pelleting properties used in experiments

	Quantities	
	Low/Small	High/Large
Moisture content	5-8 % wt	14-17% wt
Particle size	3mm	6mm
Pellet diameter	5mm	18mm

The three different pelletisation properties along with the use of two types of gasifiers constitute a group of 16 different pelletisation and gasification experiments which are shown in Table 4.2.

Table 4.2: The 16 different pelletisation processes and the type of gasifier used

Pellet type	Moisture Content (% wg)	Particle Size (mm)	Pellet Diameter (mm)	Gasifier type
1	5-8	3	5	Fluidized bed
2	5-8	6	5	Fluidized bed
3	14-17	3	5	Fluidized bed
4	14-17	6	5	Fluidized bed
5	5-8	3	18	Fluidized bed
6	5-8	6	18	Fluidized bed
7	14-17	3	18	Fluidized bed
8	14-17	6	18	Fluidized bed
1	5-8	3	5	Downdraft
2	5-8	6	5	Downdraft
3	14-17	3	5	Downdraft
4	14-17	6	5	Downdraft
5	5-8	3	18	Downdraft
6	5-8	6	18	Downdraft
7	14-17	3	18	Downdraft
8	14-17	6	18	Downdraft

Pellet unit

In Cranfield University there is a 12 kW pellet mill, assembled by "Farm Feed Systems Ltd", capable of producing pellets at a rate of 80 kg/hour, a schematic is shown in Figure 4.1. The pellet mill is ring type die (die rotates and rollers remain stationary) and contains two rollers. The feedstock is delivered in bales, and is initially shredded using a common gardener shredder to produce loose straw at approximately 5-10 cm in size. Loose straw is then fed to a hammer mill in order to decrease the size of the material even further. The decrease of the size of the material is determined by the size of screen that is inside the hammer mill.

Material is then fed into the tank through a screw conveyor. Further down the material passes through two feeding augers where water or vegetable oil can be added, before entering into the pellet mill and pellet die.

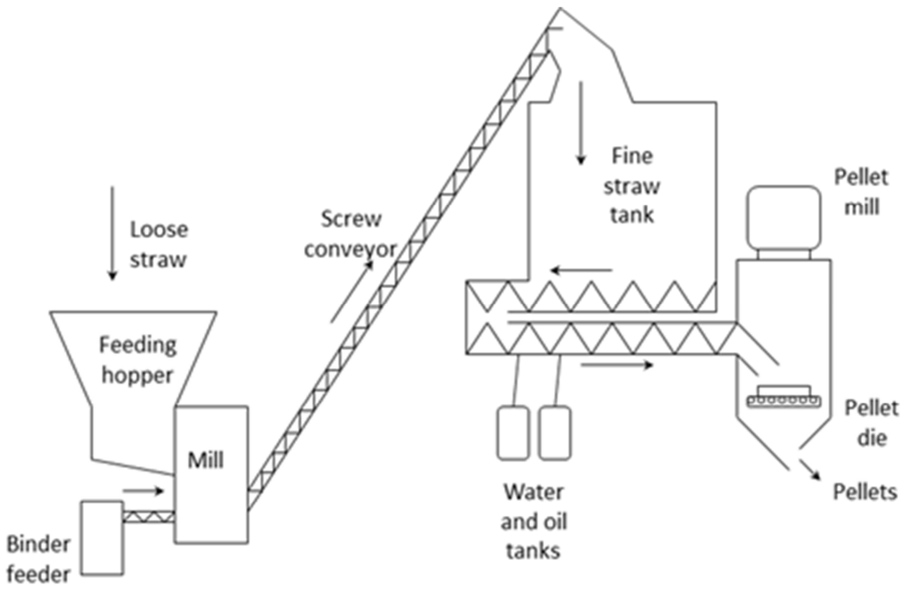

Figure 4.1: The pelleting unit

Cranfield's pelletiser was not used to manufacture the oilseed rape straw pellets as, a series of design-related issues were identified that randomised the behaviour of the pelletiser. The design limitations that were identified involve the feeding of the hammer mill, the transfer of the meal through to the main screw conveyor; the rest of the conveyors (blockages) and the feeding of the pellet die. For this reason, the pellets were manufactured by Alchemy technologies, a company in Wales. Recommendations are provided in the results and discussion of the thesis.

Pellet quality

The quality of pellets is determined in terms of the criteria shown below:

-Durability

-Mean pellet density

-Bulk density

Durability is a measure of the wearing of the pellets. The higher the durability, the lesser fines are likely to be formed during handling and/or gasifying. Heating value is the amount of heat that can be released once the pellet is combusted, measured in kJ/kg of pellets (or MJ/kg). Pellet density and bulk density are parameters that affect handling and also gasification process.

The durability of the pellets was measured by placing 500 grams of pellets into a container. The container was physically agitated 200 times and thus fines were formed. The material was then sieved in a 5mm sieve and the weight of the pellets was measured again. The method was successfully correlated with the standard methods in measuring pellet durability using three different cases with a small error (< 1.5%). The durability can be calculated as:

$$Durability = \frac{weight_{after}}{weight_{before}} \times 100 \qquad (1)$$

The bulk density of pellets was measured by placing the pellets in a $0.021m^3$ pot which later was weighed.

By measuring the mass and length of each one of the pellets and using the diameter of pellets the individual density of pellets was calculated. The mean pellet density was calculated by measuring the individual density of 15 samples and taking the mean value.

4.2 Downdraft gasification rig and process

The experimental procedure comprises a series of gasification tests undertaken in a pilot scale 75 kW_{th} downdraft gasification unit. A layout of the gasification rig is shown in Figure 4.2. The key components of the gasification rig are the main reactor; the cooling system, and finally the flare. The main reactor has a height of 2 m from the top of hopper to the grate. Inside the main reactor there is a cylindrical refractory with a height of 65cm above the grate and diameter of 24 cm. The pellets are fed in at the top of the reactor and they form a bed just above the grate as shown in Figure 4.2. The air (and/or Nitrogen) enters the reactor through four inlets, which can function independently thus allowing better control of the amount of air to be supplied and also the location in the bed where the air is supplied. The bed is fired using an igniter that is located just above the grate.

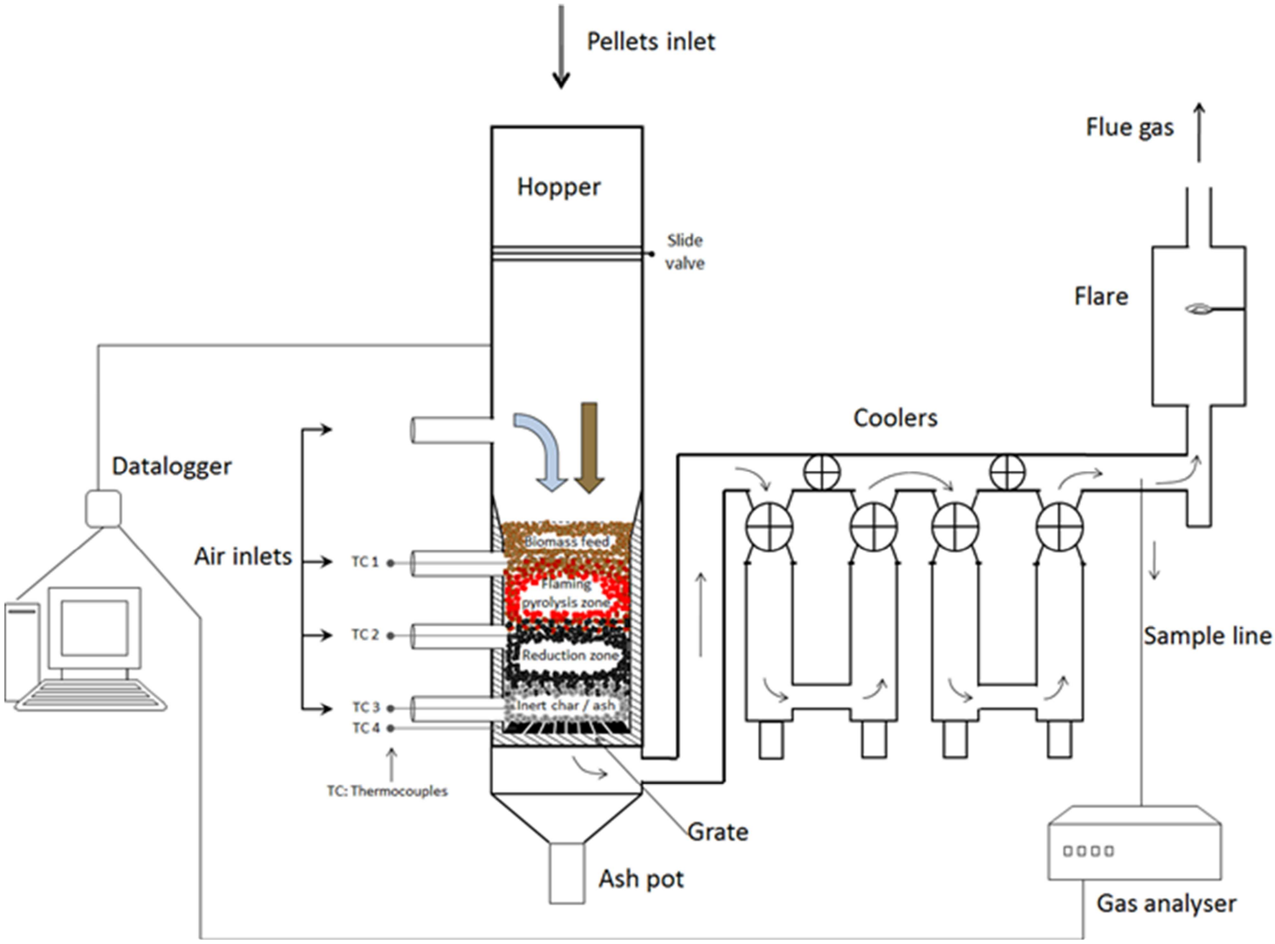

Figure 4.2: The pilot scale gasification unit

At steady state conditions, the bed forms three distinctive layers:

1. A biomass feed layer at the top of the bed, which also acts as an insulator,
2. A flaming pyrolysis zone where the material is devolatilised and also partially combusted and
3. A reduction zone where all the heterogeneous gasification reactions are taking place

As the material is dissipated, bed residues (ash and inert char), are accumulate at the lower part of the bed. Eventually the gas is formed, passing through a cooling system comprised of two coolers for the removal/condensing of tars. Downstream, a part of the gas enters a sampling line connected to two gas analysers. CO, CO_2 and CH_4 are measured by an IR gas analyser (Siemens Ultramat 2) and H_2 is measured by a thermal conductivity analyser (Siemens Calomat 2). The bulk of the gas is then burned safely at the flare before expulsion to the external environment. The temperature is monitored throughout the entire rig using type-K thermocouples.

4.3 Spouted fluidising bed gasification rig and process

The second series of tests were carried out in a pilot-scale spouted fluidised bed gasification unit (Figure 4.3). The gasifier is based on a spouted fluidised bed and can reach a thermal capacity of 50 kW_{th}. The bed material is silica sand (specifications at the end of Chapter) and the available gasifying agent is a combination of air and/or nitrogen. Air and nitrogen can be separately controlled and the mixtures vary depending on the test. Biomass pellets are fed from the top of the gasifier through a screw feeding system (feeding range: ~700 gr/h - ~22 kg/h) and air enters the unit from the bottom part. Pellets are intensely mixed in the bed with the sand, increasing the heat transfer capabilities. The product gas exits the main part of the gasifier at the top and passes through a cyclone to be cleaned of particulates and tars. Furthermore, depending on the configuration, the gas route is diverted in order for the gas to pass through a cooling system where the gas temperature drops considerably (95-120 ^{o}C) so that it can be cleaned of tars and vapours. At the far end part of the unit, the gas is burned by a flame of natural gas and air (flare). Efforts were made for the operational conditions to be the same or closely similar in all experiments.

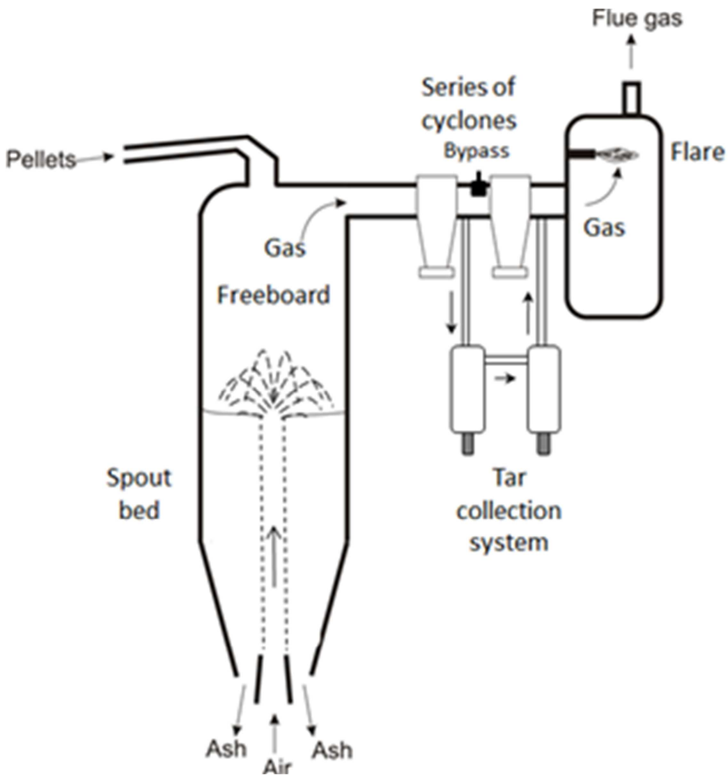

Figure 4.3: The spouted fluidised bed gasification unit

The temperature is recorded at regular (2 sec) intervals using thermocouples attached to the rig and the gas composition is analysed by the gas analysers as described in section 4.2.

The amount of sand that is fed to the spouted fluidised bed gasifier before the initiation of any experiment, weights 6.6 kg in total. The 2.5 kg out of the 6.6 kg are dropped below the spout inlet and thus the real weight of the bed is the rest above the spout inlet as we can see in Figure 4.4.

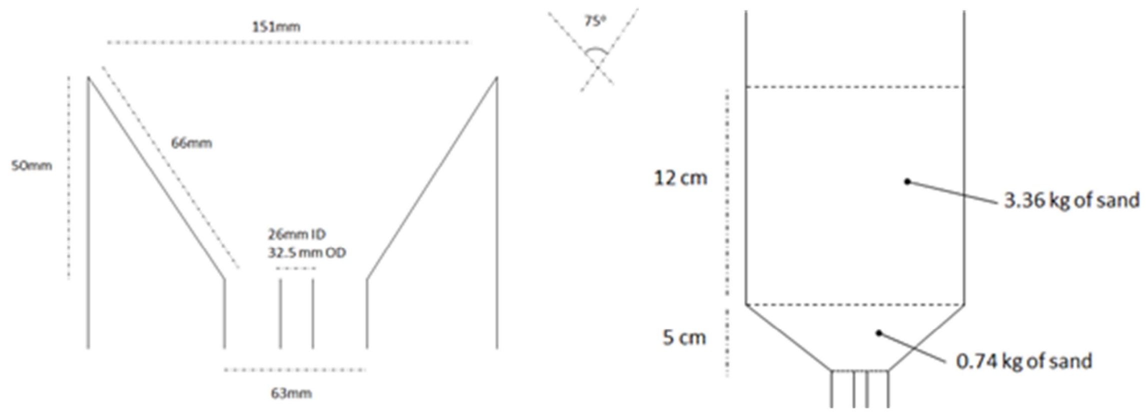

Figure 4.4: The spout dimensions and packed bed status before a test

The ash is collected in both rigs and was analysed using the Scanning Electron Microscope (Philips, XL30 ESEM) – Energy Dispersive X-ray spectroscopy (Oxford Instruments, Swift-ED) technique (SEM-EDX). The ash from the downdraft rig was collected from the ash pot below the grate although analysis was also performed on the agglomerated ash that is found on the grate. The ash from the spout bed rig was collected by sieving the bed material in a 45μm screen.

4.4 Analysis-calculations

Ultimate, proximate and ash analysis

The Ultimate and Proximate analysis of all the pellets used in the gasification tests are shown in Table 4.3 and 4.5. The OSR straw pellets made by Alchemy technologies are characterized by high content of carbon but low content of fixed carbon. The ash analysis is shown in Table 4.4

Table 4.3: Ultimate and Proximate analysis of all fuels used in the project (as-received basis)

Test method		DDGS pellets	E-On Miscanthus pellets	OSR straw pellets (low moisture)	OSR straw pellets (high moisture)
CEN/TS 15407(1)	C (%)	44.18	44.59	56	53.1
CEN/TS 15407(2)	H (%)	5.9	5.12	4.3	3.9
CEN/TS 15407(3)	N (%)	4.94	0.4	0.5	0.5
By difference	O (%)	32.95	36.89	21	23.2
CEN/TS 15407(4)	S (%)	0.52	0.01	0.25	0.25
CEN/TS 15400(5)	Cl (%)	0.18	0.01	0.5	0.5
CEN/TS 15414(6)	Moisture content (%)	7.4	10.18	8.8	10.2
CEN/TS 13039(7)	Ash (%)	3.9	2.8	8.6	8.3
CEN/TS 15418(8)	Volatile matter (%)	73.2	71.1	71.2	75.3
Calculation	Fixed carbon (%)	15.5	15.9	11.4	6.2
CEN/TS 15400(9)	HHV (MJ/kg)	18.6	18.8	19.1	19.3
CEN/TS 15400(9)	LHV (MJ/kg)	17.2	17.5	17.8	18

(1) Reproducibility SD: 0.43-5.12%wt
(2) Reproducibility SD: 0.04-1.2%wt
(3) Reproducibility SD: 0.02-0.2%wt
(4) Reproducibility SD: 0.013-0.181%wt
(5) Reproducibility SD: 0.024-0.181%wt
(6) Reproducibility SD: 0.22-0.47%wt
(7) Reproducibility SD: 0.33-3.15%wt
(8) Reproducibility SD: 1.82-4.65%wt
(9) Reproducibility SD: 0.19-1.57 MJ/kg

Table 4.4: Ash analysis

Test Method		DDGS pellets	E-On Miscanthus pellets	OSR straw pellets (low moisture)	OSR straw pellets (high moisture)
Acid digest-ICP(1)	Silica	1.01	31.58	39.7	42.1
Acid digest-ICP(2)	Aluminium oxide	0.05	3.78	15.5	14.2
Acid digest-ICP(3)	Magnesium oxide	9.23	2.95	4.3	6
Acid digest-ICP(4)	Calcium oxide	4.82	25.91	5.1	4.4
Acid digest-ICP(5)	Sodium oxide	4.34	1.14	5.5	5.8
Acid digest-ICP(6)	Potassium oxide	28.45	9.01	7.2	6.9
Acid digest-ICP(7)	Phosphorus	45.8	5.56	0.1	0.2
Acid digest-ICP(8)	Iron oxide	0.12	1.09	9.3	8.2
Elem. Anal.	Carbon	3.32	9.7	7.1	6.8

(1) Reproducibility SD: 490-23,582 mg/kg
(2) Reproducibility SD: 132-21,219 mg/kg
(3) Reproducibility SD: 81-1,932 mg/kg
(4) Reproducibility SD: 548-33,656 mg/kg
(5) Reproducibility SD: 101-1,686 mg/kg
(6) Reproducibility SD: 165-2,260 mg/kg
(7) Reproducibility SD: 50-1,716 mg/kg
(8) Reproducibility SD: 634-48,077 mg/kg

Table 4.5: Analysis of the oilseed rape straw (as-received basis)

	Oilseed rape straw
C (%)	40.81
H (%)	4.27
N (%)	0.42
O (%)	36.5
S (%)	0.24
Cl (%)	0.26
Moisture content (%)	13.4
Ash (%)	4.4
Volatile matter (%)	66.7
Fixed carbon (%)	15.5
HHV (MJ/kg)	16.2
LHV (MJ/kg)	15

Cellulose, hemicellulose and lignin content

The lignin content acts as a binder during the pelletisation process. The cellulose, hemicellulose and lignin content of the oilseed rape straw were determined. The analysis of the material was done in Aberystwyth University. The values of acid detergent fibre (ADF), neutral detergent fibre (NDF) and acid detergent lignin (ADL) were determined out of which cellulose, hemicellulose and lignin content can be calculated:

Hemicellulose = NDF – ADF

Cellulose = ADF – ADL

Lignin = ADL

Table 4.6: Analysis and determination cellulose, hemicellulose, lignin for Oilseed rape straw

Neutral Detergent fibre (%)	78.04
Acid Detergent Fibre (%)	63.97
Acid Detergent Lignin (%)	11.16

Cellulose content (%)	52.81
Hemicellulose content (%)	14.07
Lignin content (%)	11.16

(Note) Error: accuracy of equipment and measurements

Viability assessment

At the final stage viability is assessed through the parameters shown below:

- **Gas composition**
- **Gas yield**
- **Gas Higher Heating Value**
- **Cold gas efficiency**
- **Carbon conversion efficiency**
- **CO/CO_2 ratio**
- **Mass Conversion Factor**
- **Specific energy rate**
- **Gasification rate**

A product gas that would be assessed as good quality gas, is the one that would have high yield (especially high yield of $CO + H_2 + CH_4$), the higher possible HHV (cannot be that high in air gasification, around 4±0.5 MJ/m^3 or higher would be considered good), high cold gas efficiency (usually higher than 30-40%, indicating not only that the pellets were of high quality, but also that the entire gasification process it was done by the highest standards possible), and high carbon conversion efficiency, usually higher than 50-60%, that would point out the dissipation of carbon through the gasification process and its transformation into a combustible gas. In addition, good gas quality would require the CO/CO_2 ratio to be higher than unity (indicating good conversion of CO_2 to CO which means good efficiency of the Boudouard reaction) and the highest possible mass conversion factor (higher than 0.5 would be considered as good quality). Specific energy rate and gasification rate both can be used to compare tests in gasifiers with different dimensions. The method that was used to calculate these parameters and explain them is the nitrogen balance. The equations of the methodology are derived from the literature [96-100]. The nitrogen balance proof of the equations is written by the author.

The nitrogen balance

The mass balance in the gasification process can be achieved by applying the method of the nitrogen balance. The basic idea is that the amount of nitrogen in the input would be the same as the nitrogen in the output. The nitrogen balance equations shown in the boxes are used in order to quantify the syngas output. The results of these equations are used later to complete the mass balance and the analysis of the gas.

n_i: moles of species

MW_i: molar weight of species

nf_i: molar (or volume) fraction of species

mf_i: mass fraction of species

We have in the output of the gas stream (syngas):

$$nf_{N2\_output} = \frac{n_{N2\_output}}{n_{GAS}} = \frac{\dfrac{m_{N2\_output}}{MW_{N2}}}{\dfrac{m_{GAS}}{MW_{GAS}}} \Rightarrow nf_{N2\_output} = \frac{\dfrac{mf_{N2\_output} * m_{GAS}}{MW_{N2}}}{\dfrac{m_{GAS}}{MW_{GAS}}} \Rightarrow$$

$$\Rightarrow nf_{N2\_output} = \frac{mf_{N2\_output} * MW_{GAS}}{MW_{N2}} \Rightarrow \boxed{mf_{N2\_output} = nf_{N2\_output} * \frac{MW_{N2}}{MW_{GAS}}}$$

Using the equation above, is possible to calculate the mass fraction of any species in the syngas provided that the molar fraction of the species is known.

During the gasification process, the nitrogen in the air (or any additional) does not participate in the conversion reactions, and thus, the amount of the nitrogen in is equal to the amount of the nitrogen out.

$$n_{N2\_input} = n_{N2\_output}$$

So one can write:

$$nf_{N2\_output} = \frac{n_{N2\_output}}{n_{GAS}} = \frac{n_{N2\_input}}{n_{GAS}}$$

And thus:

$$nf_{N2\_output} = \frac{n_{N2\_input}}{n_{GAS}} = \frac{\frac{m_{N2\_input}}{MW_{N2}}}{\frac{m_{GAS}}{MW_{GAS}}} \Rightarrow nf_{N2\_output} = \frac{m_{N2\_input} * MW_{GAS}}{m_{GAS} * MW_{N2}} \Rightarrow$$

$$\Rightarrow m_{GAS} = \frac{m_{N2\_input} * MW_{GAS}}{nf_{N2\_output} * MW_{N2}}$$

But from the latter proof: $nf_{N2\_output} = \frac{mf_{N2\_output} * MW_{GAS}}{MW_{N2}}$, and thus continue as:

$$m_{GAS} = \frac{m_{N2\_input} * MW_{GAS}}{\frac{mf_{N2\_output} * MW_{GAS}}{MW_{N2}} * MW_{N2}} \Rightarrow \boxed{m_{GAS} = \frac{m_{N2\_input}}{mf_{N2\_output}}}$$

Using the equation above, is possible to calculate the total mass of the syngas provided that we have already calculated the mass fraction of nitrogen in the syngas.

The molar weight of the syngas can be calculated as the sum of mole fractions of species multiplied the molecular weight of the according species:

$$\boxed{MW_{GAS} = \sum_{i}^{N} nf_i * MW_i}$$

Using the nitrogen balance the total mass of the syngas (or mass flow rate) and the nitrogen in the syngas was calculated. The same rule can be applied to the rest of the syngas species to calculate their masses too.

$$\boxed{m_i = mf_i * m_{GAS} = \frac{nf_i * MW_i}{MW_{GAS}} * m_{GAS}}$$

For example:

$$m_{CO} = \frac{nf_{CO} * MW_{CO}}{MW_{GAS}} * m_{GAS}$$

Carbon balance

The total carbon in the syngas can be calculated as:

$$m_{C\_output} = MW_C * \left(\frac{m_{CO}}{MW_{CO}} + \frac{m_{CO_2}}{MW_{CO_2}} + \frac{m_{CH_4}}{MW_{CH_4}} \right)$$

The amount of carbon in the syngas that was derived only by the fuel is:

$$m_{C\_output\_fuel} = m_{C\_output} - m_{C\_injected}$$

Using the above equation the Carbon Gas Yield Factor or Carbon Conversion Efficiency, CCE, (different names in different sources for the same thing) can be calculate which is the amount of carbon in the gas, that was only derived from the fuel, over the initial amount of carbon in the fuel:

$$\text{Carbon conversion efficiency} = \frac{m_{C\_output\_fuel}}{m_{C\_fuel}}$$

The mass of the injected carbon could be derived from the injection of CO_2.

Oxygen balance

The total oxygen in the syngas can be calculated as:

$$m_{O_2\_output} = MW_{O_2} * \left(\frac{\frac{1}{2} * m_{CO}}{MW_{CO}} + \frac{m_{CO_2}}{MW_{CO}} \right)$$

The amount of oxygen in the syngas that was derived only by the fuel is:

$$m_{O_2\_output\_fuel} = m_{O_2\_output} - \left(m_{O_2\_air} + m_{O_2\_injected} \right)$$

Similar as before the oxygen gas yield factor which is the amount of oxygen in the syngas that was derived only by the fuel over the total oxygen in the fuel, can be calculated as:

$$\text{OCE} = \frac{m_{O_2\_output\_fuel}}{m_{O_2\_fuel} + m_{O_2\_fuel\_water}}$$

The mass of the injected O_2 could be derived from injection of CO_2 or steam. The mass of oxygen in the fuel can be taken from the Ultimate analysis of the fuel and the mass of oxygen in the fuel water can be derived from the Proximate analysis.

Hydrogen balance

The total hydrogen in the syngas can be calculated as:

$$m_{H_2\_output} = MW_{H_2} * \left(\frac{m_{H_2}}{MW_{H_2}} + \frac{2 * m_{CH_4}}{MW_{CH_4}} \right)$$

The amount of hydrogen in the syngas that was derived only by the fuel is:

$$m_{H_2\_output\_fuel} = m_{H_2\_output} - m_{H_2\_injected}$$

And the hydrogen gas yield factor, which is the amount of hydrogen in the syngas that was derived only by the fuel, over the hydrogen in the fuel:

$$\text{HCE} = \frac{m_{H_2\_output\_fuel}}{m_{H_2\_fuel} + m_{H_2\_fuel\_water}}$$

So, now the mass conversion factor can be calculated which is the total mass of fuel that was converted into gas over the amount of fuel that can be converted

$$\text{mass conversion factor} = \frac{m_{C\_output\_fuel} + m_{O_2\_output\_fuel} + m_{H_2\_output\_fuel}}{m_{C\_fuel} + m_{O_2\_fuel} + m_{H_2\_fuel} + m_{O_2\_fuel\_water} + m_{H_2\_fuel\_water}}$$

The thermal conversion efficiency can be also calculated which is a ratio between the chemical enthalpy of the fuel and feedstock and can give information about the efficiency of the conversion from solid to gas:

$$\text{thermal conversion efficiency} = \frac{m_{GAS} * LHV_{GAS}}{m_{fuel} * LHV_{fuel}}$$

Where LHV is the lower heating value in MJ/kg

Since the m_{GAS} have been already calculated it is possible to calculate the volume flow of the gas Q_{GAS}. Once this is done the gas yield is calculated which is the volume of syngas over the total mass of the fuel (including the ash).

$$Yield_{GAS} = \frac{Q_{volumetric}}{m_{fuel}}$$

where Q_{GAS} is the volumetric flowrate in m^3/h

The higher heating value of the gas (in MJ/m^3) can be calculated using the following equation:

$$HHV_{GAS} = \frac{12.75 * H_2 + 12.63 * CO + 39.82 * CH_4}{100}$$

where, the species in these equations denote volumetric percentages (the results that are obtained by the gas analysers).

In order to validate the calculations, two equations can be used to calculate the cold gas efficiency (same as the thermal conversion efficiency) and a second method for the carbon conversion efficiency (same as the carbon gas yield factor)

$$CGE = \frac{Yield_{GAS} * HHV_{GAS}}{HHV_{fuel}}$$

$$CCE = \frac{12 * Yield_{GAS} * (CO + CO_2 + CH_4)}{22.4 * C} * 100$$

where, C is the carbon content in the fuel

A comparison between different gasification rigs could be made using the two following equations. The specific energy rate (MJ/m^2*h) is a measure of the production of energy within the cross section of a gasifier and the gasification rate (kg/m^2*h) is a measure of the amount of gas that was produced within the cross section of a gasifier.

$$\text{Specific Energy Rate} = \frac{Q_{volumetric} * HHV_{GAS}}{A}$$

$$\text{Gasification Rate} = \frac{m_{C\_output\_fuel} + m_{O_2\_output\_fuel} + m_{H_2\_output\_fuel}}{A}$$

Minimum spouting velocity

Before starting with the tests in the spouting fluid bed, the minimum spouting velocity needs to be identified. In order to do that, certain sand properties should be known (Table 4.7). The sand that is used in the spout bed is a "Garside 16/30 Yellow" and the major chemical elements that it is composed of are shown in Table 4.8. The sand belongs to the groups B and D of the Geldart classification (particle characterization according to their fluidization behaviour) [101] which mean that it is appropriate for fluid and spout beds.

Table 4.7: Sand properties

Particle surface diameter (mm)	0.5
Specific gravity (g/cm^3)	2.65
Uncompacted bulk density (g/cm^3)	1.56
Shape	Sub-angular to rounded

Table 4.8: Chemical analysis of sand; Major elements

ELEMENT	%
Silica	98.29
Alumina	0.31
Titania	0.02
Iron	1.29

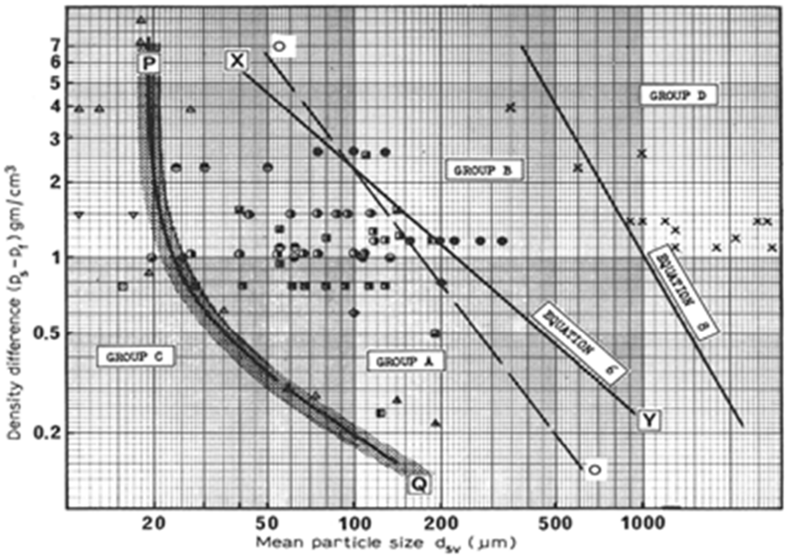

Figure 4.5: The Geldart classification [6]

The minimum spouting velocity was calculated using the Mathur and Gishler correlation [92]:

$$U_{ms} = \left(\frac{d_{particle}}{d_{bed}}\right) * \left(\frac{d_{spout}}{d_{bed}}\right)^{1/3} * \left[2 * g * H * \left(\frac{\rho_{particle} - \rho_{air}}{\rho_{air}}\right)\right]^{1/2}$$

Where, $d_{particle}$ is the diameter of the particle, d_{bed} is the diameter of the bed, d_{spout} is the inner diameter of the spout air inlet, g is the gravitational acceleration, H is the height of the bed, $\rho_{particle}$ and ρ_{air} are the densities of the particle and the air respectively (in STP).

4.5 Accuracy and error

Ultramat 2

The basic functioning principle of Ultramat is the molecule absorption of bands of infra-red (IR) radiation which is specific for every different type of molecule. The IR radiation is emitted from a source and passes through a sample chamber into which the gas is flowing. The sample chamber holds three layers of energy detectors out which the first one absorbs energy form the centre of the sample and the other two absorb energy from the periphery of the sample. Thus, the gas concentration is calculated. The Ultramat 2 is used to calculate the CO, CO_2 and CH_4. The error is less than 1% of the full scale value.

Calomat 2

The calomat is a thermal conductivity gas analyser. The basic functioning principle is the different thermal conductivity of the gases. The analyser operates by using a silica chip of which the measuring diaphragm contains thin film resistors. The resistors are regulated at constant temperature. The gas concentration is calculated by using the magnitude of an electric current value that depends on the sample gas. The error in this analyser could reach the maximum of 5% and it is mainly due to the influence of interfering gases.

Pico thermocouples

The main operating principle of the thermocouples is that the voltage that is generated in the junction between two metals is a function of temperature. The type K thermocouple produces a voltage which changes by $40\mu V/^{o}C$ with a resolution of $1/40^{o}C$. A well-functioning thermocouple has very small error and high accuracy of $0.3\%x0.5^{o}C$ (or $0.0015^{o}C$ per $0.5^{o}C$ error or $\pm1.2^{o}C$ at $800^{o}C$).

Rotameters

The rotameter is a type of flowmeter and its function is based on the variable area principle which consists of 3 basic parts. These parts are a uniformly tapered tube, a floating object and the measuring scale. The rotameter is usually placed vertically with the smaller diameter of the tube at the bottom which acts as the inlet. The floating object is inside the tube and has a diameter equal to the inlet of the tube. The passing of a gas causes the object to float and the higher the float is, the more gas is passing through the tube due to the increased diameter of the tube. The accuracy of the rotameter is mainly dependent on the accurate calibration in terms of pressure, temperature and flow control. A good rotameter has an error no larger than 2% (assuming that the fluid pressure, temperature etc remain constant). A typical rotameter does not have an error larger than 5%.

Spout-bed screw feeding system

The major errors from the screw feeder are the observational errors in combination with the bulk errors. The screw feeder at each different setting requires a specific amount of time to complete a complete revolution. The timings were measured and the connection of these timings with the kgs was established. The SD for the timings was also calculated and thus an error can be calculated in kg for the input biomass feed. The error for the feeding system is reported as SD in kg and can be found in the tables of the following chapters.

Downdraft feeding technique

The downdraft gasifier is fed from the top in batches and thus every so often the lid at the top of the gasifier was open in order to feed. Due to the batch like process, the feeding depends on the type of pellet and the air injected into the gasifier due to the different consumption rate at different air flows for different type of pellets. Thus it is safe to assume that a part of the feeding's technique error would be the error of the rotameters (less than 5%). Another part of the error would be the calculative error which is difficult to calculate for the OSRS due to the lack of adequate number of repeat tests using similar process parameters.

Pellet density, bulk density, durability, pellet length

The error for the pellet density was also calculated. The SD was taken using 15 samples and this error could be observed in the graphs concerning pellet density that can be found in the following chapters. No error was calculated for bulk density and durability. The error for the pellet length was calculated using the standard deviation for 40 samples.

5 The pelleting process

In this chapter the effect of the pelleting process on the quality of pellets is going to be presented and discussed. Initially data concerning the quality of the pelleting process itself are shown such as the current used by the mill and the temperature of the die. Secondly the latter data are related with the quality of the pellets as presented in Chapter 4. In turn, the quality data are related with the gasification process to deduct which parameters mostly affect the gasification process.

5.1 Pelleting process results

The following tests were conducted by Alchemy Technologies Limited as instructed by the author. The report that was sent includes graphs of the electric current (measured in Ampere) that was used by the mill in order to successfully complete the tests, which is an indirect measure of the friction between the feedstock and the die and of the pressure that was needed for each test. The report also includes the log of each test.

The aim was to investigate the effect of extreme values of moisture content (5-8% and 14-17%) and particle size (3 mm and 6 mm) on the pelleting process using extreme die sizes (5 mm and 18 mm). As have been reported by Alchemy Technologies, the initial instruction of using the 15 mm die could not be satisfied because the pellet mill could not process the material due to the high extrusion ratio of the die that was proved too aggressive to process the material without additives and consequently the overheat that was caused. The complete series of tests is shown in Table 5.1.

Table 5.1: The complete series of OSRS tests performed by Alchemy Technologies Limited

No. of test	**MC**: Feedstock moisture content (% wg)	**PS**: Mill particle size (mm)	**DD**: Die diameter (mm)	Quantity (kg)
1	5-8	3	5	100
2	5-8	6	5	100
3	14-17	3	5	100
4	14-17	6	5	100
5	5-8	3	18	100
6	5-8	6	18	100
7	14-17	3	18	100
8	14-17	6	18	100

5.1.1 Manufacturing method

The straw was delivered in Alchemy Technology in bales that were passed through a Christy 30 kW hammer mill with slotted screen in order to break the material in about 50 mm pieces. Further down the process, the chopped straw was processed through a Christy mill of 7 kW using a 5 mm and a 10 mm grid. The 5 mm grid produced a meal of around 3 mm particle size and the 10 mm grid produced a meal of around 6 mm particle size as reported. Before each run the average moisture content was determined using 3 samples in an Adam 300 halogen moisture balance. Water was added in the meal to the tests 3, 4, 7 and 8 in order to increase the moisture up to the required level as instructed. Finally the meal was used in a pellet mill CPM 45 kW intermediate laboratory press with a modified feed in system. The two different dies used, have the same extrusion ratio equal to 8/1.

5.1.2 The 5 mm die tests

The pellet types 1-4 were manufactured using the 5 mm die. In test 1 the material was initially fed slowly so that the pressure in the die would be built reaching high electric current (amps) and a die temperature of around 50^{o}C to be achieved. As have been reported a small amount of oil (less than 1% wt) was injected only in the warm-up period into the pelleting chamber to avoid overheating and blockages. The warm-up period consumed the 15 kg of the feed. After the warm-up period pellets were produced satisfactorily but the feed rate needed to be kept low because the pressure and friction due to the low moisture of the feed was high and the current were increasing rapidly, also increasing the die temperature with an increase of the feed rate. Near the end of the run the die temperature reached around 90^{o}C and blockages in the die holes had started to form. Nevertheless, the test was complete with no further problems.

In order to start feeding the type 2 material the die temperature was cooled to around 45^{o}C. The test started well but after the first half period the die temperature rapidly increased to near 85^{o}C and smoke was observed. The smoke was formed due to the high friction in the die holes, which started to char the surface of the pellets. Thus, a small amount of oil had to be injected to reduce the friction, however the current (Amperes, indirect measure of pressure and friction) had already risen and the die blocked. A small fire followed. The fired was quenched and some parts of the pellet mill were removed to avoid damage and the die was allowed to cool down before continuing the test. Similar problems appeared in the second trial and further problems in the third trial damaged some of the equipment. Nevertheless in 3 trials the material was successfully pelletised, however a lot of problems were encountered.

Figure 5.1: Type 1 and 2 of OSRS (oil seed rape straw) pellets

The difference in the performance of the first two tests occurred due to the particle size. The pellet mill used additional current in order to further reduce the size of the 6 mm feed inside the die and thus additional friction forces appeared resulting in an increase of the temperature (Figure 5.3) and thus overheating the die. In Figure 5.2 we can see the current that was used by the mill for the tests 1-4 and there, a small difference in the current between tests 1 and 2 can be observed. Perhaps additives had to be injected (such as water or oil) from the beginning of the test 2 in order to avoid the problems. Pictures of the first two produced types of pellets are shown in Figure 5.1.

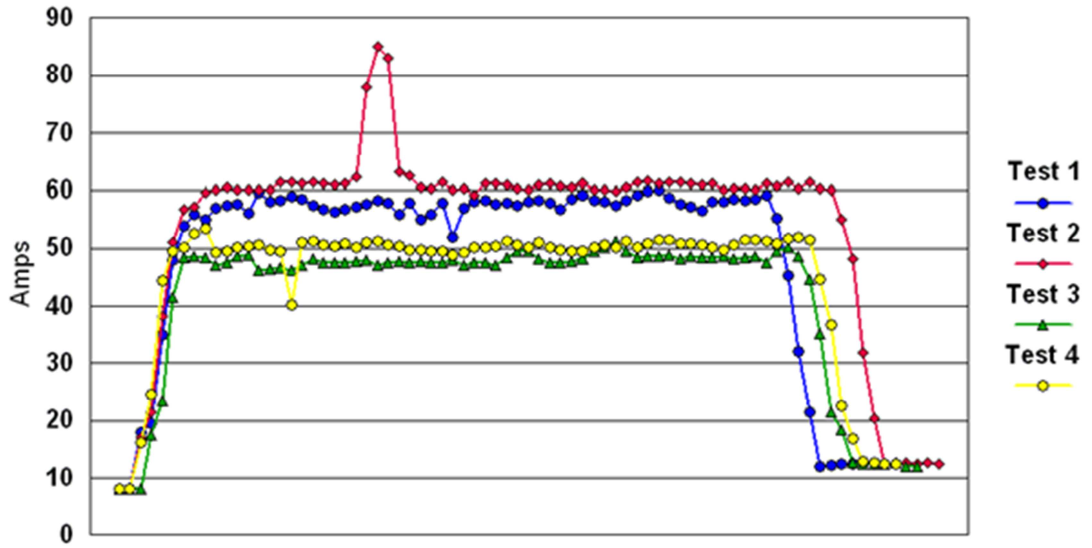

Figure 5.2: The electric current used by the mill for the tests 1-4 (An indirect measure of pressure and friction) with time scale from 90-120 minutes

The practical issues observed in test 1 and 2 were reduced in test 3. The higher moisture content acted as a lubricant and the test progressed without fault. Interesting observations included the large amount of steam that was produced in the run and the “fir-tree” effect which is usual in feeds with high moisture. The “fir-tree” effect most likely occurred due to the rapid expansion of the pellet, from the steam that was formed, once it exited the die hole. Similar effects were observed in test No.4 although slightly higher current was required once more, compared to test No.3, due to of the larger particle size.

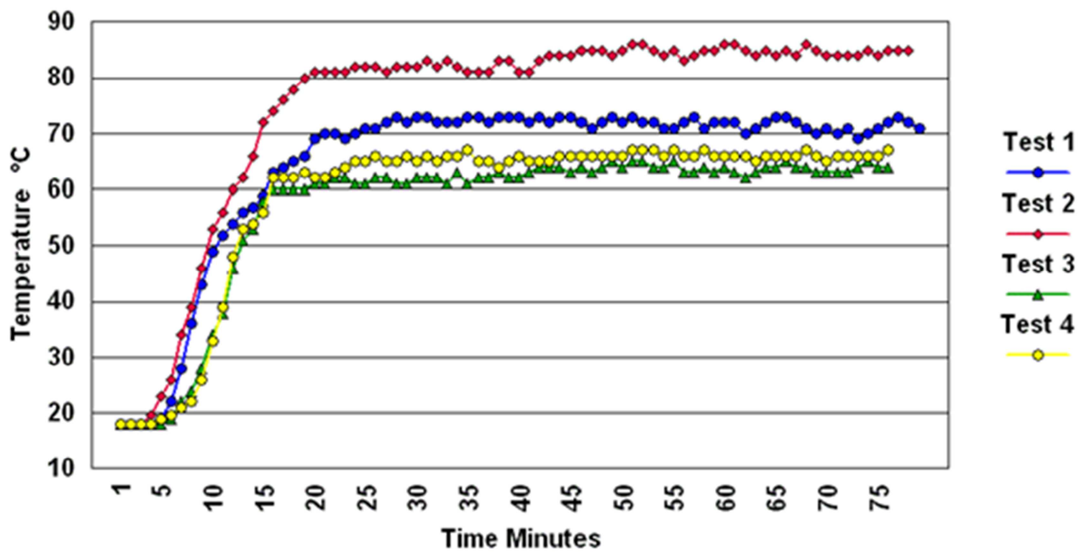

Figure 5.3: Die temperature for tests 1-4

In overall terms for the first four tests, higher current was required for the dry pellets compared to the wet ones and higher current was required for the larger particle size feed compared to the one with small particle size feed. Higher current was observed testing the dry, large particle size feed (test 2) and the smallest current was observed testing the wet, small particle size feed (test 3). The dry feed was more difficult to control and it is thought that the addition of a considerable amount of oil (2-3% wt) in the beginning of the test may have prevented the problems that arose. Pictures of type 3 and 4 of pellets can be seen in Figure 5.4.

Figure 5.4: Type 3 and 4 of OSRS pellets

5.1.3 The 18 mm die tests

The pellet types 5-8 were manufactured using the 18 mm die. In test 5 the feed of the material was progressed more slowly due to the previous experience with the smaller diameter dry pellets that caused problems. Initially good and strong pellets were produced although the current was high (Figure 5.6) and the temperature continued to rise (Figure 5.7) despite the small amount of oil that was initially injected (<2% wt). After the first half of the test, a sudden increase of load, overloaded and jammed the pelletiser. The pelletiser was opened and allowed to cool down at around 40^{o}C. In the second trial similar problems arose but this time due to the high current that led to high temperatures, fire was produced and the process was shut down for repairs and maintenance. Despite the problems, the pellets that were produced initially in the first and second trial were enough to be tested later on to the gasifier.

In test 6 the moisture was slightly increased to avoid the problems that occurred in test 5. Furthermore a small amount of oil was also injected (<1% wt) for similar reasons and no problem occurred although the current was still high.

Practically, there was no difference in the pelleting behaviour between tests 5 and 6 despite the different feed particle size. Pictures of the two types of pellets are shown in Figure 5.5. The difference in amps that can be seen between the two tests in Figure 5.6 is due to the injection of small amounts of water and oil

Figure 5.5: Type 5 and 6 of OSRS pellets

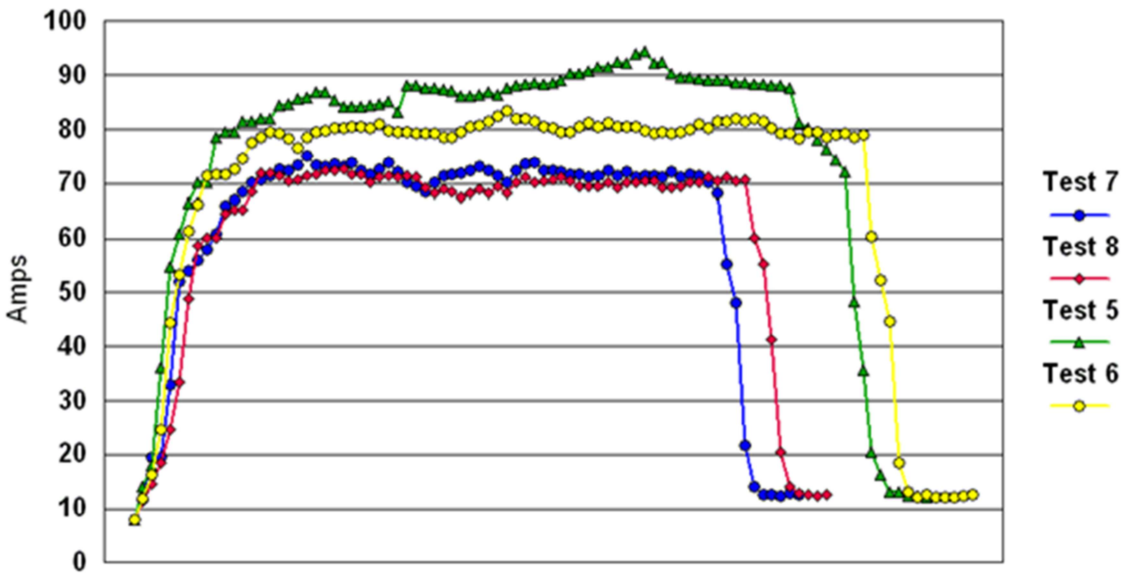

Figure 5.6: The electric current used by the mill for the test 5-8 (An indirect measure of pressure) with time scale from 90-120 minutes

In the test 7 the pelleting process occurred without major problems although the pellets were shorter, more friable and with slightly less strength in comparison to the previous types. Once the die warmed up, the current level remained stable until the end.

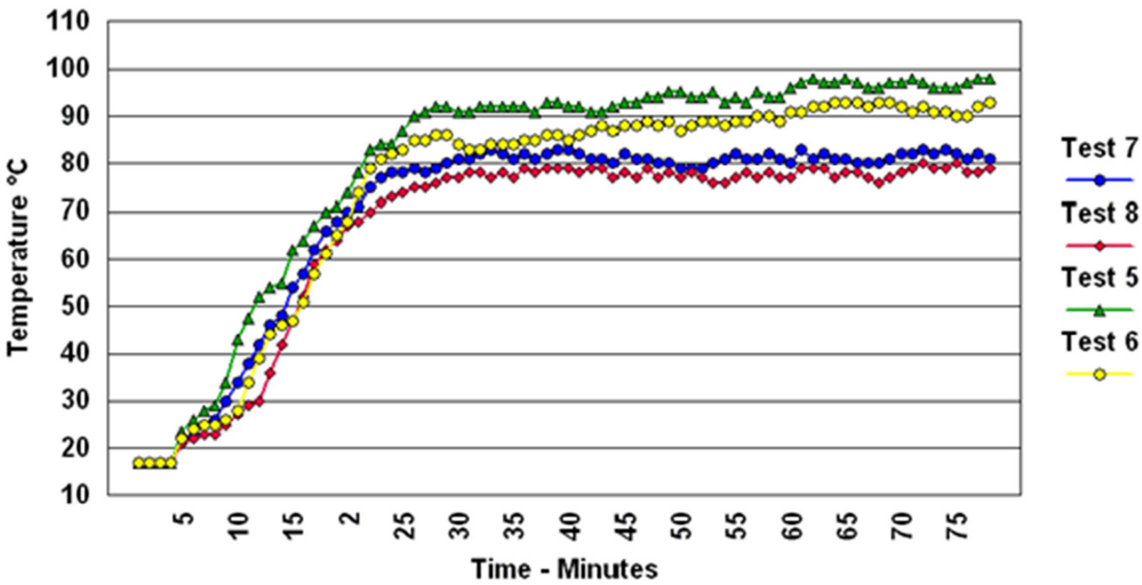

Figure 5.7: Die temperature for tests 5-8

Test 8 was similar as the previous test. The die was allowed to cool down to about 40^{o}C and after the initial feed of material the current once more was stabilized. The pellets that were produced were also friable and less strong in comparison to the previous types but the process in general was easier to control and no problems appeared. Pictures of pellets produced from tests 7 and 8 are shown in Figure 5.8

Figure 5.8: Type 7 and 8 of OSRS pellets

The test 7 and 8 showed that in the case of the 18 mm diameter dies, the particles size was not affecting the process. The feed was further reduced in size, inside the pellet mill, using the 5 mm die however it was not further reduced using the 18 mm diameter die. That explains why the level of current in tests 7 and 8 is the same. The differences between the tests 5 and 6 can be only attributed to the additional injection of small amounts of water and oil in test 6. Furthermore the effect of moisture content can be observed once more in the 18 mm die tests as was also observed in the 5 mm die. The wet feed used smaller current in comparison to the dry feed and that can be attributed to the lubricant behaviour of moisture. Pictures of all the pellets together are shown in Figure 5.9.

Figure 5.9: An apparent comparison between the 8 types of OSRS pellets

5.2 Effect of pelleting parameters on pelleting process

The pelleting parameters have a fundamental effect on the pelleting process. The pelleting parameters under investigation are the moisture content, the particle size and the die diameter. All three parameters and their combinations have affected the manufacturing process of pellets, though not all in equal weight. The two important indicators, that point out the impact of the pelleting parameters in the pelleting process, are the amount of Amperes used by the pellet mill and the die temperature. Both of the two values represent the friction that was applied between the feedstock and the die. If there is a high friction factor, then the pellet mill requires more energy in order to process the material and thus, due to the friction, the die temperature rises. This is shown in Figure 5.10. The higher current and temperature in the process were observed during the utilization of the large diameter die because the die holes are longer in comparison to the ones in the smaller die. The friction between the feedstock and the die depends mainly on the lubricant characteristics of the feedstock i.e. the addition of oil or moisture can decrease the friction factor.

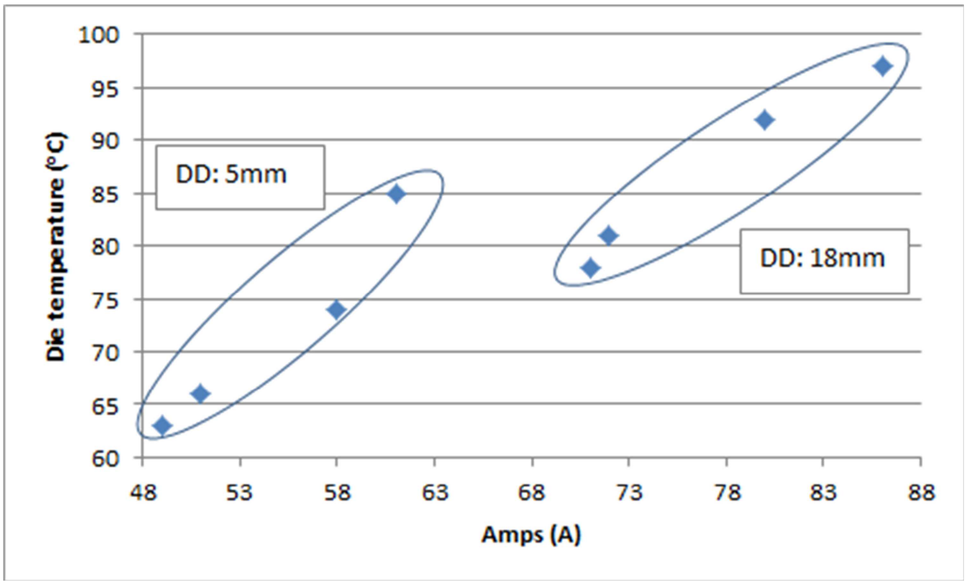

Figure 5.10: The relation between the pellet mill electric current and the die temperature

5.2.1 Effect of moisture content on the pelleting process

The moisture content is one of the fundamental parameters in the pelleting process. The effect of moisture content on the current used by the pellet mill is shown in Figure 5.11. In all cases, the moisture content acts as a lubricant, by decreasing the current required by the pellet mill, regardless of the size of the chop or the diameter of the die.

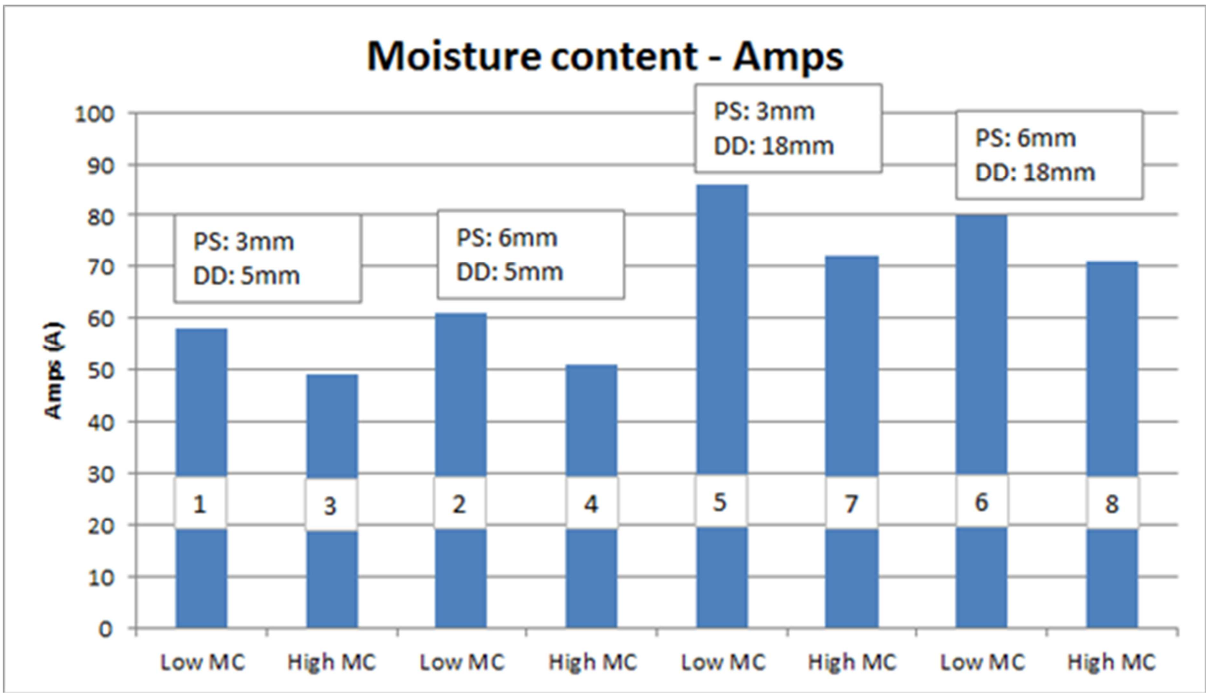

Figure 5.11: The effect of moisture content on the electric current required by the pellet mill

Similar effect was observed for the feedstock moisture content on the die temperature (Figure 5.12). The increasing moisture content decreased the friction factor between the die and the feedstock, leading to a decreased dissipation of energy by the pellet mill and lower temperature of the die. The steam formed, in the case of the high moisture tests, further contributed to the decreased temperature in comparison to the dry feedstock.

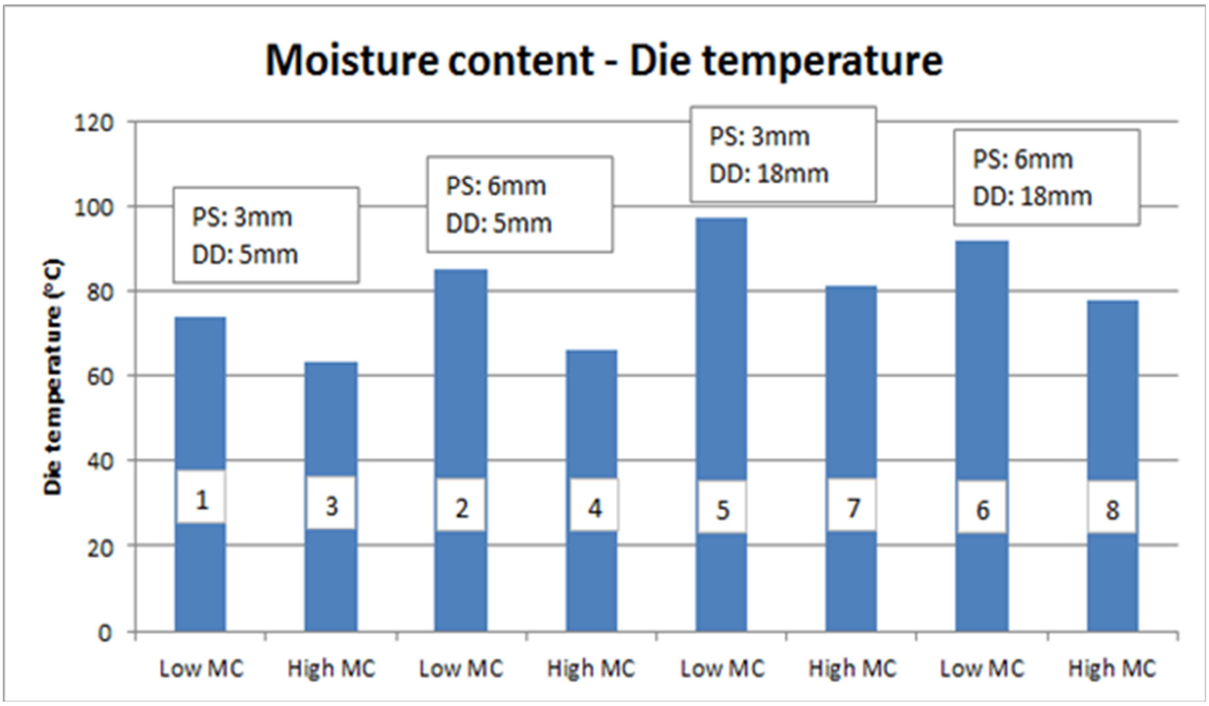

Figure 5.12: The effect of moisture content of the die temperature

5.2.2 Effect of particle size on the pelleting process

The particle size slightly affected the pelleting process when using the 5 mm diameter die however did not affect the process when using the 18 mm diameter die. The 3 mm particle size could fit into the 5 mm die hole however the 6 mm particle size could not fit into the 5 mm die hole. Thus, further size reduction occurred inside the die reducing the 6 mm particles into smaller ones. For that reason extra energy required by the pellet mill to reduce in size the 6 mm particles so that could fit inside the 5 mm die. This effect is shown in Figure 5.13 (pairs “1,2” and “3,4”). The extra energy required by the pellet mill led to an increase in the friction and thus an increase in the temperature inside the die which can be seen in Figure 5.14 (pairs “1,2” and “3,4”). The effect could not be observed when using the 18 mm die. That is because both the 3 mm and 6 mm particle size could fit inside the 18 mm die hole; thus no further particle size reduction occur inside the die. The small differences observed in pairs

“5,6” and “7,8” could be attributed to the addition of small amounts of oil and water as mentioned previously.

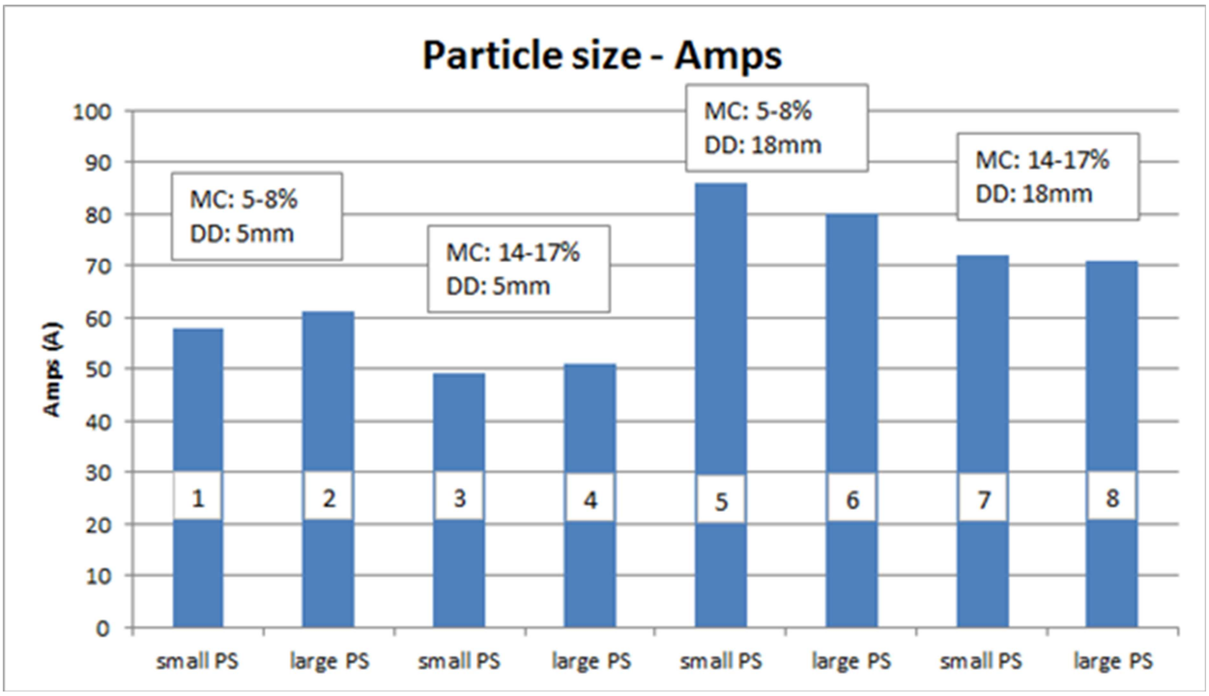

Figure 5.13: The effect of particle size on the electric current required by the pellet mill

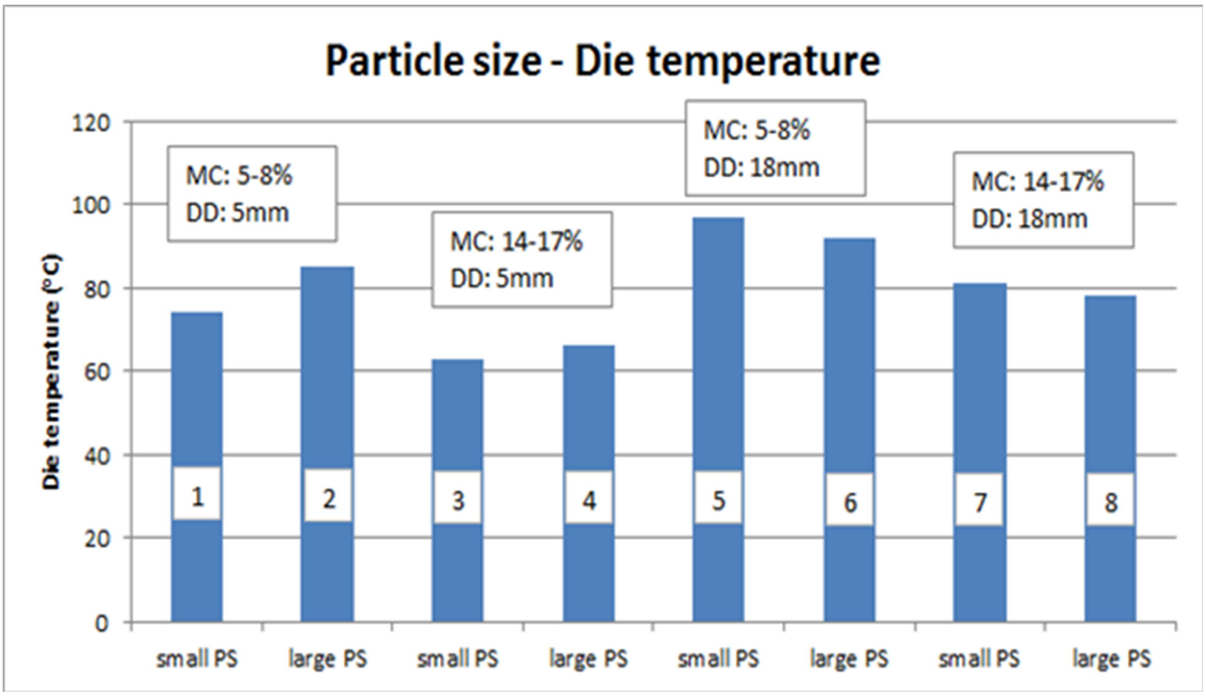

Figure 5.14: The effect of particle size on the die temperature

5.2.3 Effect of die diameter on the pelleting process

The die diameter has a clear effect on the current required by the pellet mill. In Figure 5.15 a clear relation is shown between all pairs. The tests using the die with the larger diameter required higher current in all cases, when compared with the tests using the smaller diameter die. This effect can be accredited to the longer die holes of the large diameter die. Due to the longer holes, a larger amount of feedstock remained inside the die hole for an extended period of time thus increasing the friction factor despite the fact that the extrusion ratio of both dies is the same (8/1).

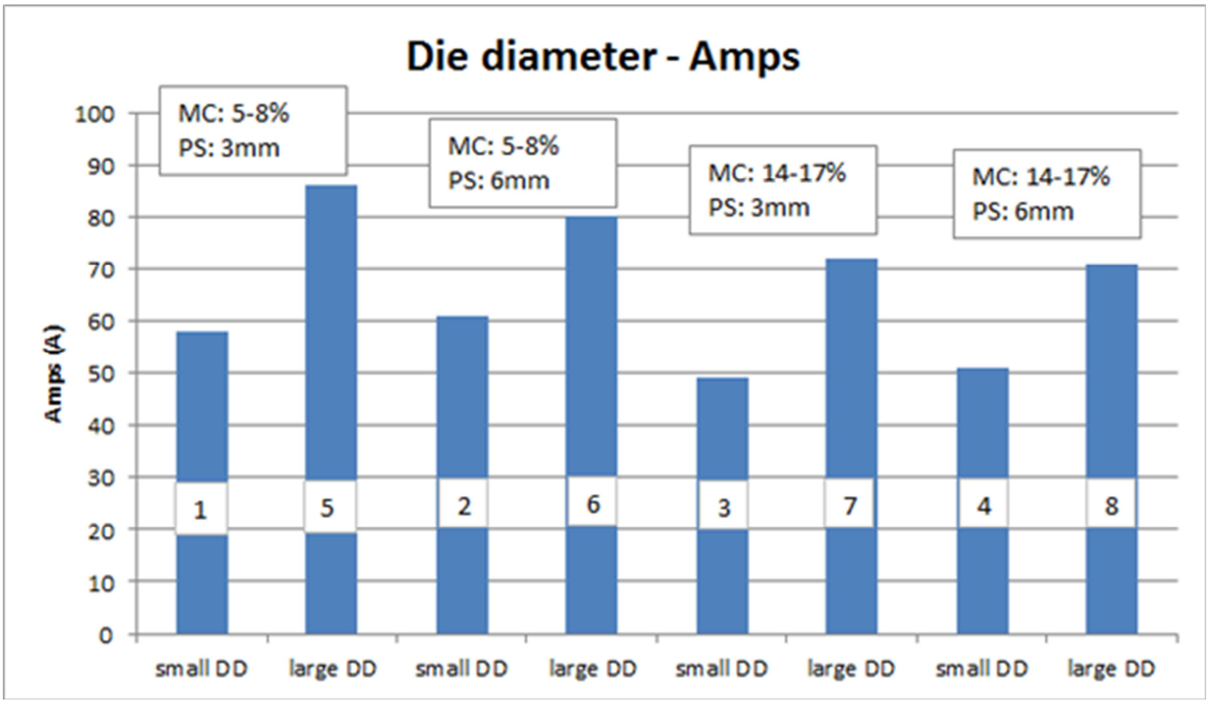

Figure 5.15: The effect of die diameter on the electric current required by the pellet mill

The die diameter has a similar effect to the die temperature as with the current. For the same reasons as in the former case, the temperature of the die is increased by increasing the die diameter.

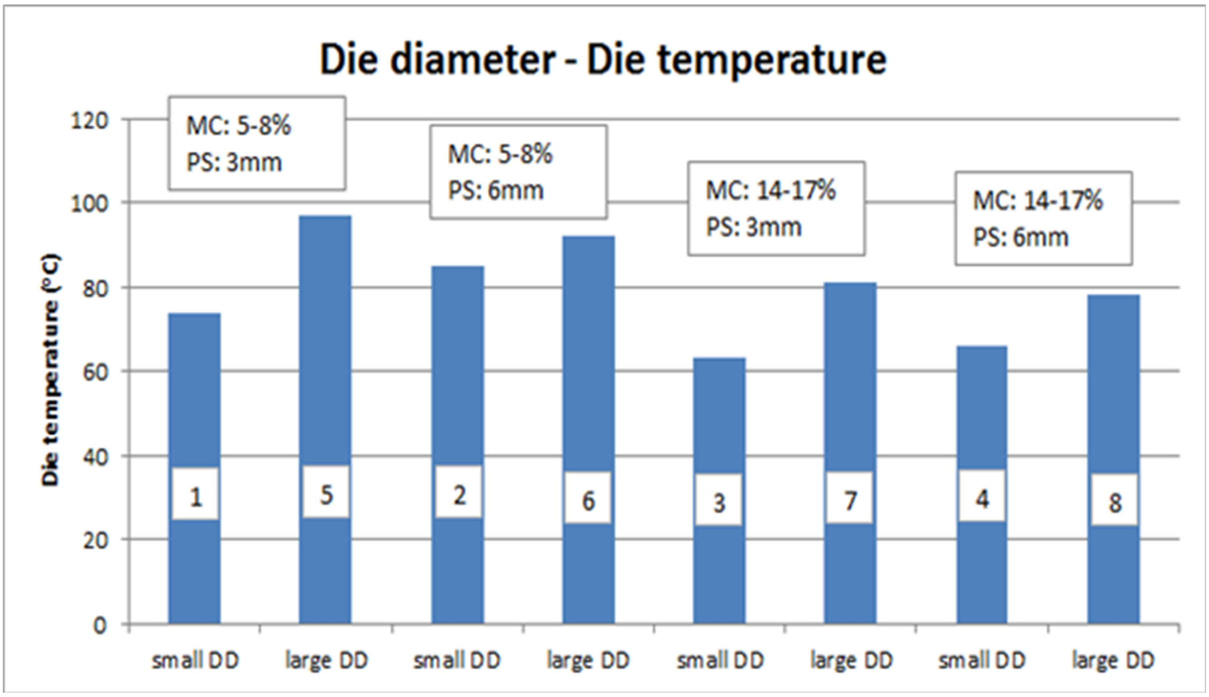

Figure 5.16: The effect of die diameter on the die temperature

5.3 The relationship between the pelleting process and the pellet quality

The pelleting process properties have a profound effect on the quality of the pellets. This section will discuss this effect. The quality analysis of the pellets is shown in Table 5.2. The quality assessment parameters are the mean pellet density, the bulk density and the pellet durability. The swelling of the pellets is also shown in Table 5.2 (pellet size), the nominal die diameter is shown inside the brackets, the actual mean pellet diameter after the pellets exit from the die, is shown outside the brackets. In addition, the properties of the pelleting process have an effect on the mean pellet length as it is shown in Figure 5.17. The smallest mean pellet length was observed in type 3 pellets and the largest in type 5 pellets.

Table 5.2: Quality analysis of pellets

Type of pellet	Mean pellet density (kg/m^3)	Bulk density (kg/m^3)	Durability (%)	Pellet size (mm), brackets: nominal diameter
OSRS pellets 1	902(±101)	498	93.4	6.4 (5)
OSRS pellets 2	958(±68)	498	93.1	6.4 (5)
OSRS pellets 3	1065(±112)	417	87	6.4 (5)
OSRS pellets 4	1029(±107)	403	87.3	6.4 (5)
OSRS pellets 5	1192(±71)	638	94.7	21 (18)
OSRS pellets 6	1105(±107)	570	95	21 (18)
OSRS pellets 7	1249(±115)	624	94.2	21 (18)
OSRS pellets 8	1213(±134)	565	94	21 (18)
DDGS pellets	1248(±60)	686	91	6.3
E-On Miscanthus pellets	1187(±40)	645	96.5	8

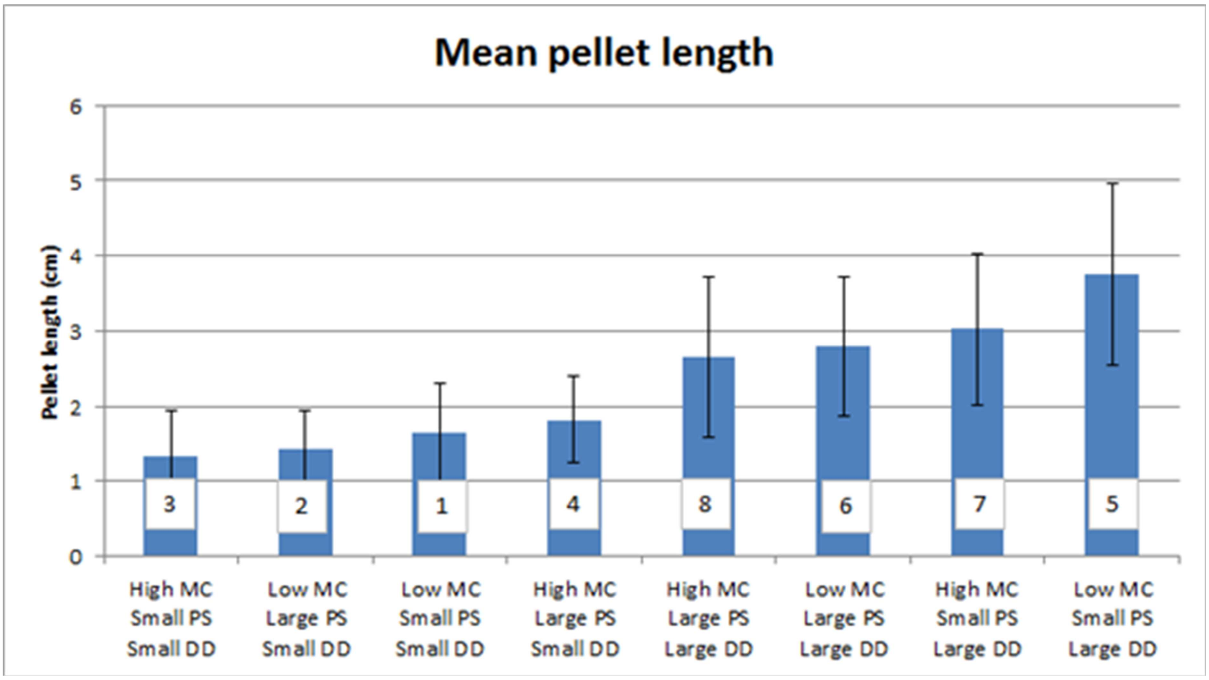

Figure 5.17: The mean pellet length for each one of the pelleting tests (bars: SD)

5.3.1 The relationship between the pelleting process and the pellet density

The relationship between the current required by the pellet mill and the pellet density is shown in Figure 5.18. Distinguishing the data between the two die diameters, it is clear to say that the increased current is related with decreased pellet density. In both cases the wet feed resulted in a higher pellet density in comparison to the dry feed. Due to the absence of moisture there were high friction factors during the process of the dry feed reaching high current without the benefit of high compression. Although it seems logical that by increasing the current thus by increasing the compression that is applied to the feedstock by the pellet mill, it should have resulted in an increase of the pellet density, this was not the case. This is because the different pelleting properties (moisture content, particle size) affected the pelleting process itself and thus the current required by the pellet mill (the current is a value dependent on the pelleting properties); which means that the extra current that was dissipated was a result of the different pelleting properties that were used; in this case the absence of moisture that would have acted as a lubricant lowering the current required.

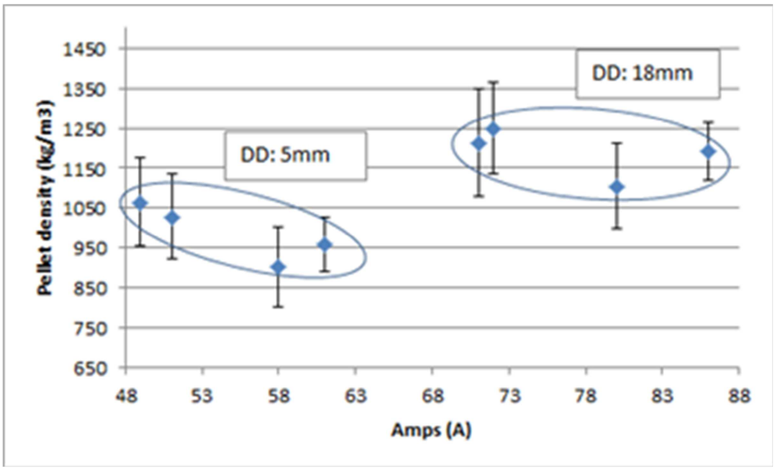

Figure 5.18: The relationship between the current and the pellet density

The relationship between the die temperature and the pellet density (Figure 5.19) was similar to the previous case, the relationship between the current and the pellet density. The pellet density decreased with an increase of the die temperature for both die sizes. The increased temperature in the dry feed was a result of a high friction between the feed and the die due to the absence of sufficient amounts of moisture.

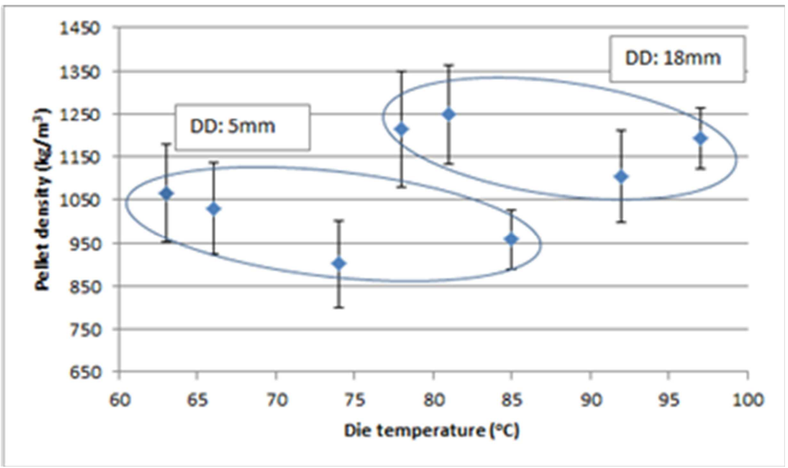

Figure 5.19: The relationship between the die temperature and the pellet density

5.3.2 The relationship between the pelleting process and the bulk density

Generally the increased current is related with greater bulk density in both die diameters as shown in Figure 5.20. At 5 mm die diameter, the bulk density is significantly greater at higher current, whereas in 18 mm die diameter there is no notable increase in the bulk density across the range of current presented.

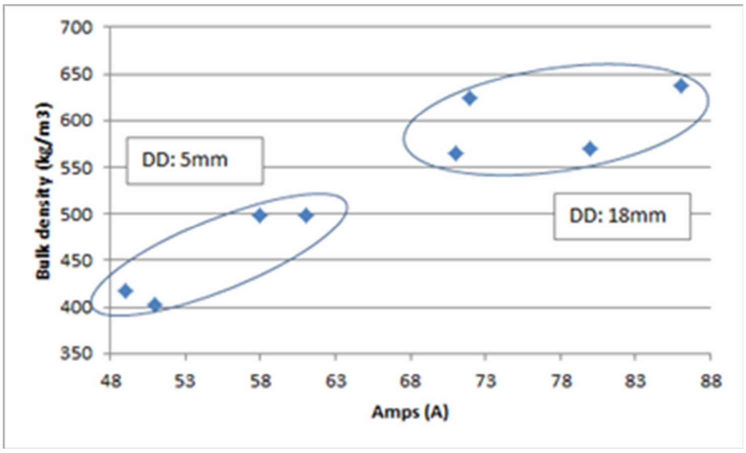

Figure 5.20: The relationship between the current and the bulk density

Similar relations were observed in the relationship between the die temperature and the bulk density as shown in Figure 5.21.

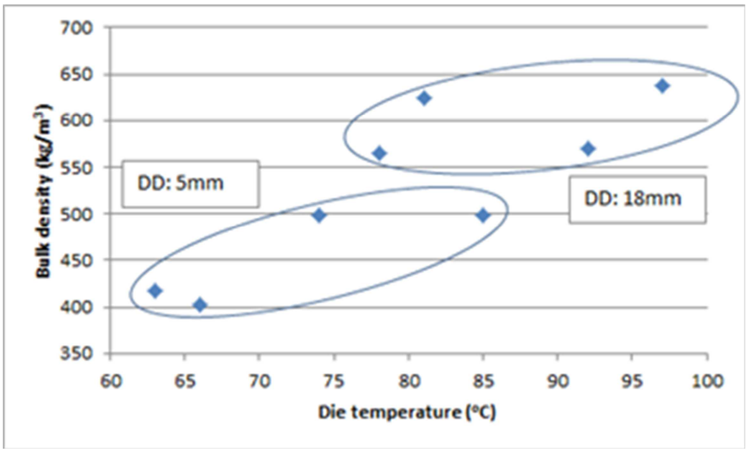

Figure 5.21: The relationship between the die temperature and the bulk density

5.3.3 The relationship between the pelleting process and the pellet durability

The relationship between the pelleting process and the pellet durability is similar to the above cases. In the Figure 5.22, in the case of the 5 mm diameter die the durability is rapidly increased with an increase in the current but in the case of the 18 mm diameter die the increase in the durability is less rapid. As discussed previously, in the case of the 18 mm diameter die, the increase is less rapid due to the addition of small amounts of oil in order to prevent the formation of fire and smoke.

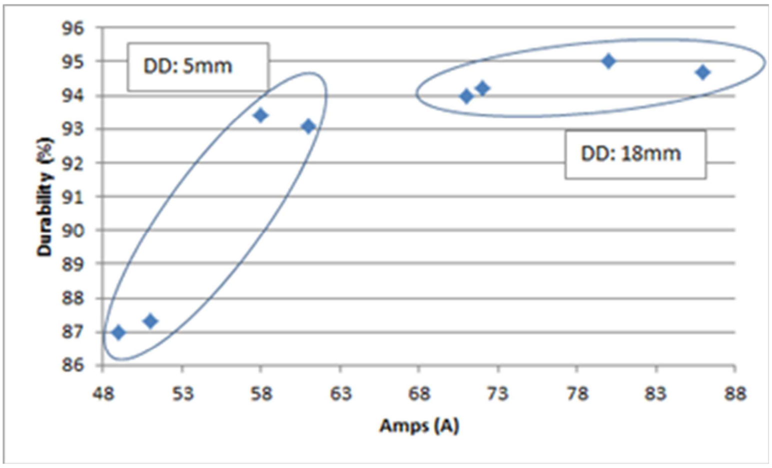

Figure 5.22: The relationship between the current and the pellet durability

The relationship between the die temperature and pellet durability is shown in Figure 5.23. It is observed, a rapid increase of the durability in the 5 mm diameter die and a steady increase in the 18 mm diameter die. The temperature is a direct indicator of the friction applied between the feed and the die and thus it can be concluded that the increase of the friction factor also increases the pellet durability.

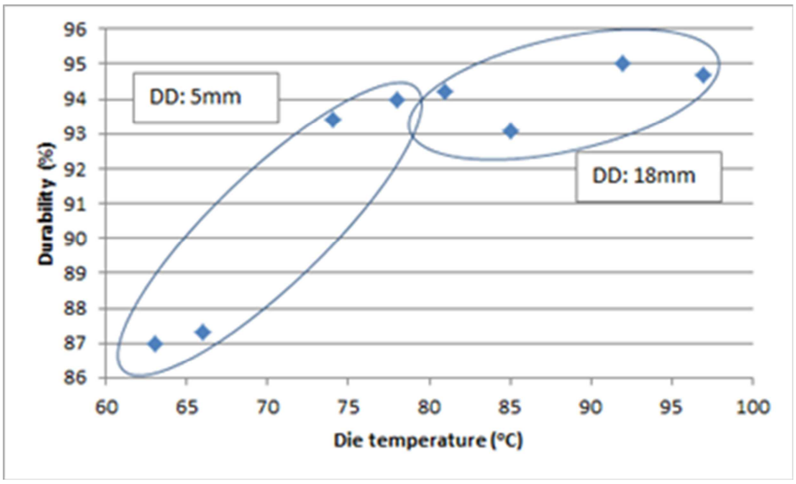

Figure 5.23: The relationship between the die temperature and the pellet durability

Generally the results reported in the previous three sub-chapters show that an observed increase in the current means that pellets of lower pellet density, higher bulk density and higher durability are yielded in both cases of small and large diameter dies. Similarly an increase of the die temperature means the production of pellets again with lower pellet density and higher bulk density and durability. Interestingly, there is a clear relationship of the

1) pelleting parameters with the pelleting process ;
2) pelleting process with the quality of pellets;
3) pelleting parameters with the quality of pellets;

5.4 Effect of pelleting parameters on pellet quality

The effect of pelleting parameters directly on the pellet quality is presented in this section. The pelleting parameters discussed are the feedstock moisture content, the particle size of the chop and the diameter of the die. The pellet quality is assessed by means of mean pellet density, bulk density and pellet durability. The results will allow the prediction of pellet quality after every pelleting process.

5.4.1 Effect of feedstock moisture content on pellet quality

The feedstock moisture content has a fundamental impact on the quality of the pellets. The effect of feedstock moisture content on the mean pellet density is shown in Figure 5.24. In each case, the higher feedstock moisture content resulted in a higher pellet density. This is due to the fact that the moisture content acts as a binder between the feedstock particles due to capillary pressure and interfacial forces. Furthermore, the effect was of equal weight in both small diameter and large diameter die.

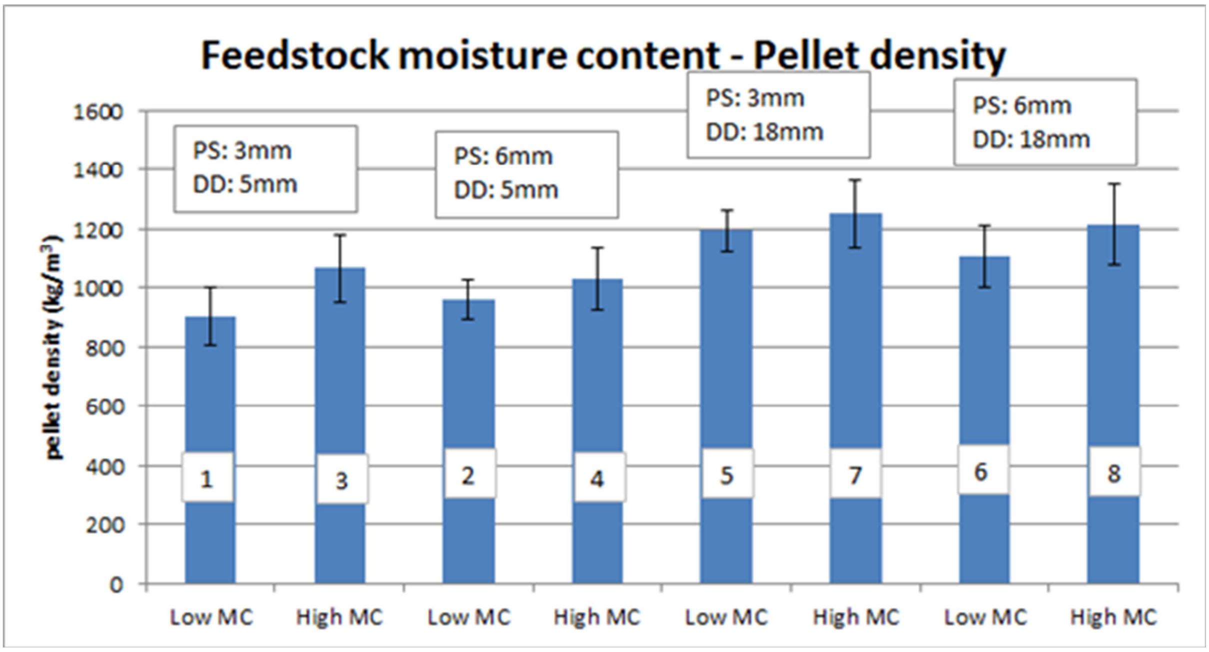

Figure 5.24: The effect of feedstock moisture content on the mean pellet density

The feedstock moisture content also has an impact upon the bulk density of the pellets which is shown in Figure 5.25. For all pairs the bulk density of the pellets decreases with an increase of the moisture content. The effect is more prominent on the test that used the 5 mm diameter die (pairs “1,3” and “2,4”). On the other hand, on the tests that used the 18 mm diameter die (pairs “5,7” and “6,8”) the impact was of a lesser weight. This could be attributed to the high temperatures that were observed during the tests that used the 18 mm diameter die, and in turn led to the evaporation of a large portion of moisture, thus decreasing the effect of moisture upon the process. The effect is also prominent on the pair “6,8” however this is due to the addition of oil in test 6 increasing the lubricant characteristics and thus decreasing the pellet density.

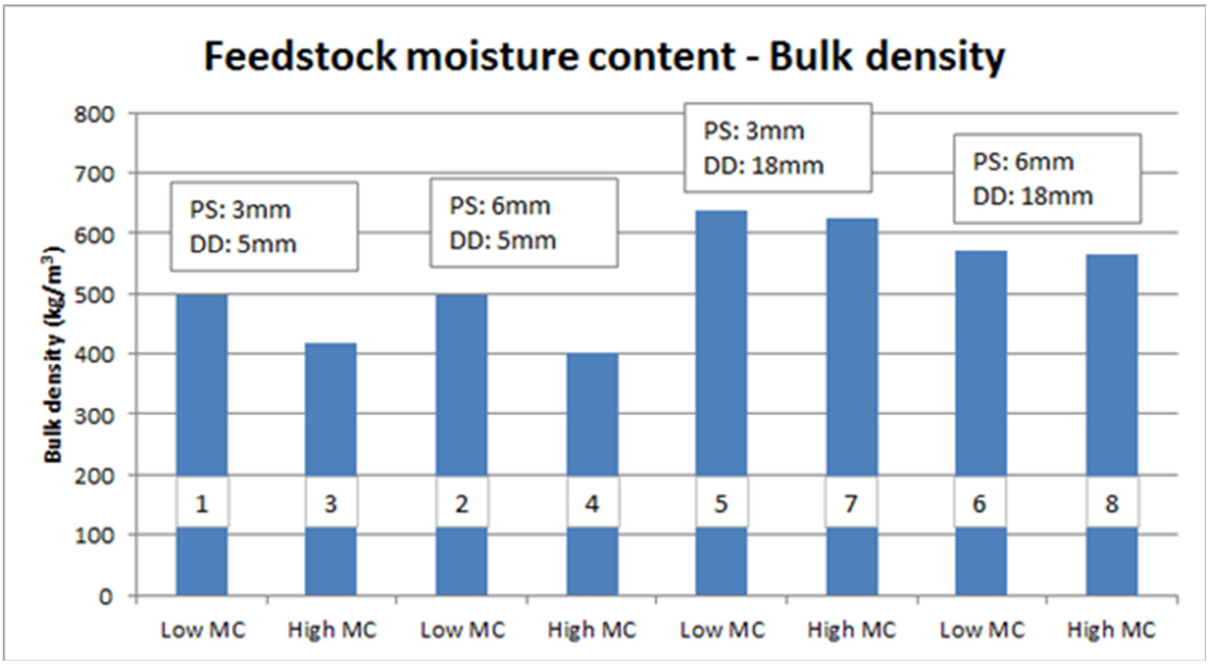

Figure 5.25: The effect of feedstock moisture content on the bulk density

The feedstock moisture content has an effect on the durability of the pellets, in which the pellet durability decrease with higher moisture content. This is highlighted in Figure 5.26. This is likely to be due to the increased moisture content which resulted in larger spaces between the chopped particles, and due to the incompressibility of water the particles could not bind together in an efficient manner. The phenomenon is more apparent in the tests which used the 5 mm diameter die and less apparent in the tests that used the 18 mm diameter die. Again, this could be attributed to the high temperatures that were observed during the tests 7 and 8 and in turn resulted in a higher durability pellets. It may also be attributed to the addition of small amounts of oil in tests 5 and 6 that reduced the friction and thus the durability of the pellets.

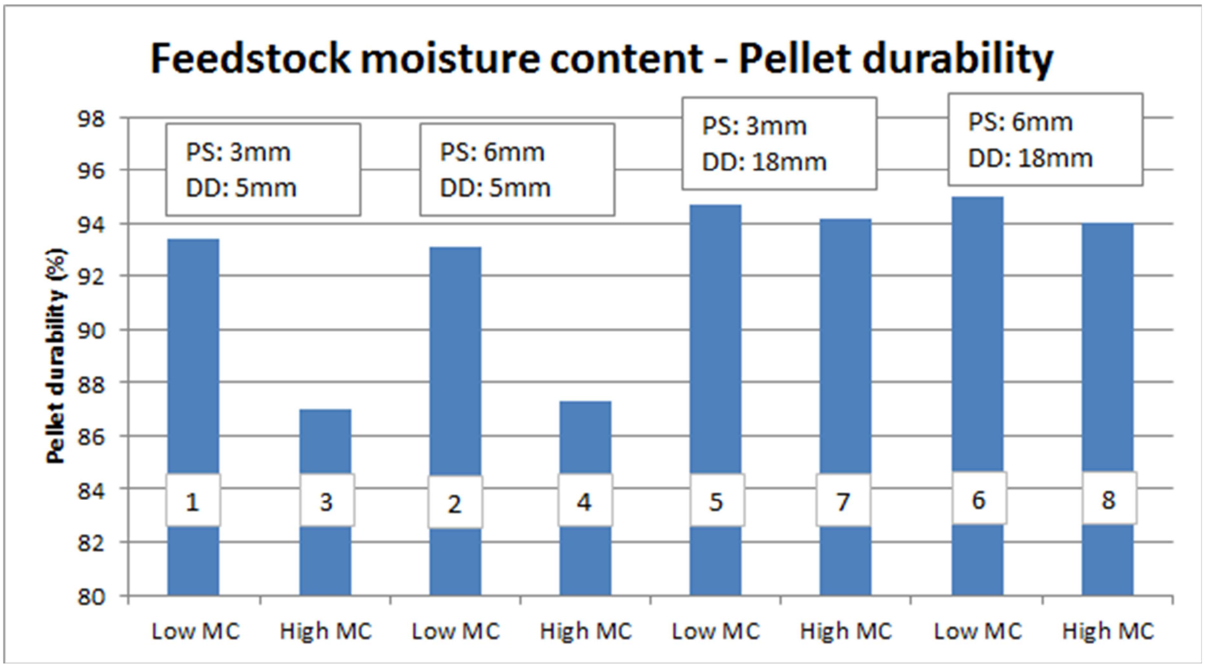

Figure 5.26: The effect of feedstock moisture content on the pellet durability

5.4.2 Effect of feedstock particle size on pellet quality

The feedstock particle size had an effect upon the quality of the pellets which is shown in Figure 5.27. In the most cases the increased particle size resulted in a decrease of the pellet density, which is due to the small particles occupying all available empty spaces in the bulk and thus increasing the density. In test 1, however, this phenomenon could not be observed. Furthermore, the impact was higher in the tests that used the 18 mm diameter die (tests 5-8) because the large chop was not further reduced in size as with the tests 2 and 4. It is likely that this internal size reduction in the tests 2 and 4 resulted in increased temperatures as shown in previous sections and in turn the increased temperature was the cause of an increase in the pellet density.

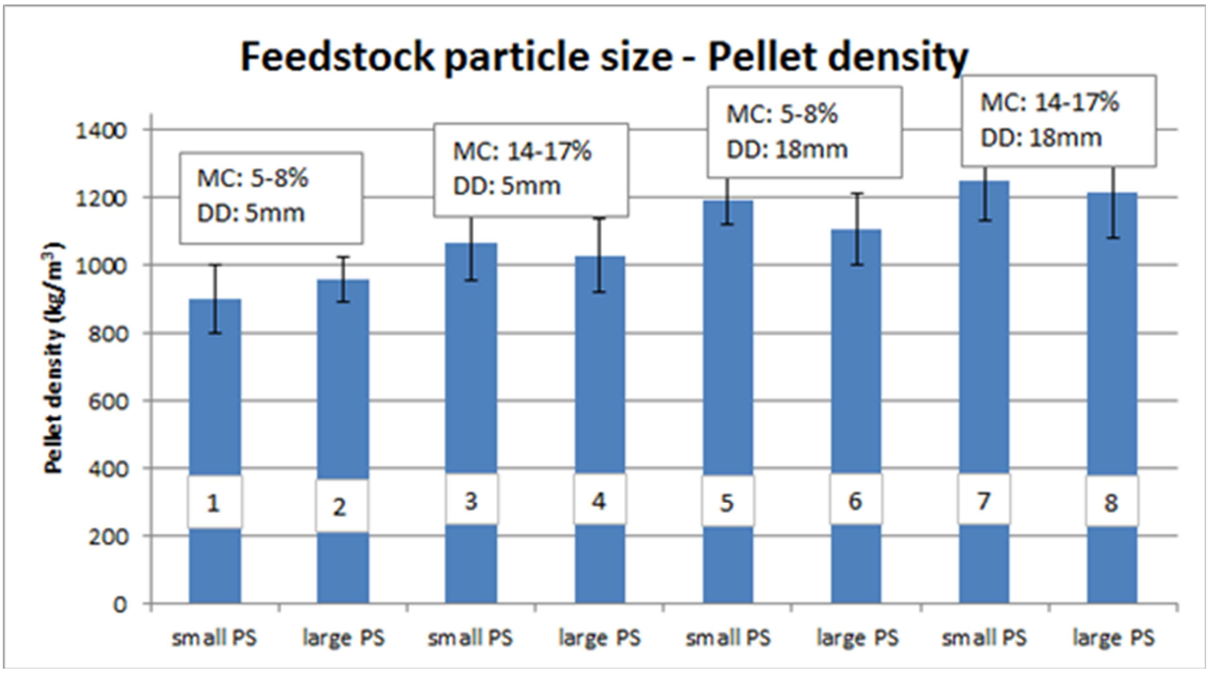

Figure 5.27: The effect of feedstock particle size on the mean pellet density

The feedstock particle size has also an effect upon the bulk density of the pellets but this is only significant in the tests which used the 18 mm diameter die (tests 5-8) as we can see in Figure 5.28. Otherwise, in tests 1-4 this phenomenon could not be observed possibly due to the further size reduction of the large chop inside the small die and that in its turn led to chop of equal size. An effect of feedstock particle size upon the pellet durability could not be detected (Figure 5.29).

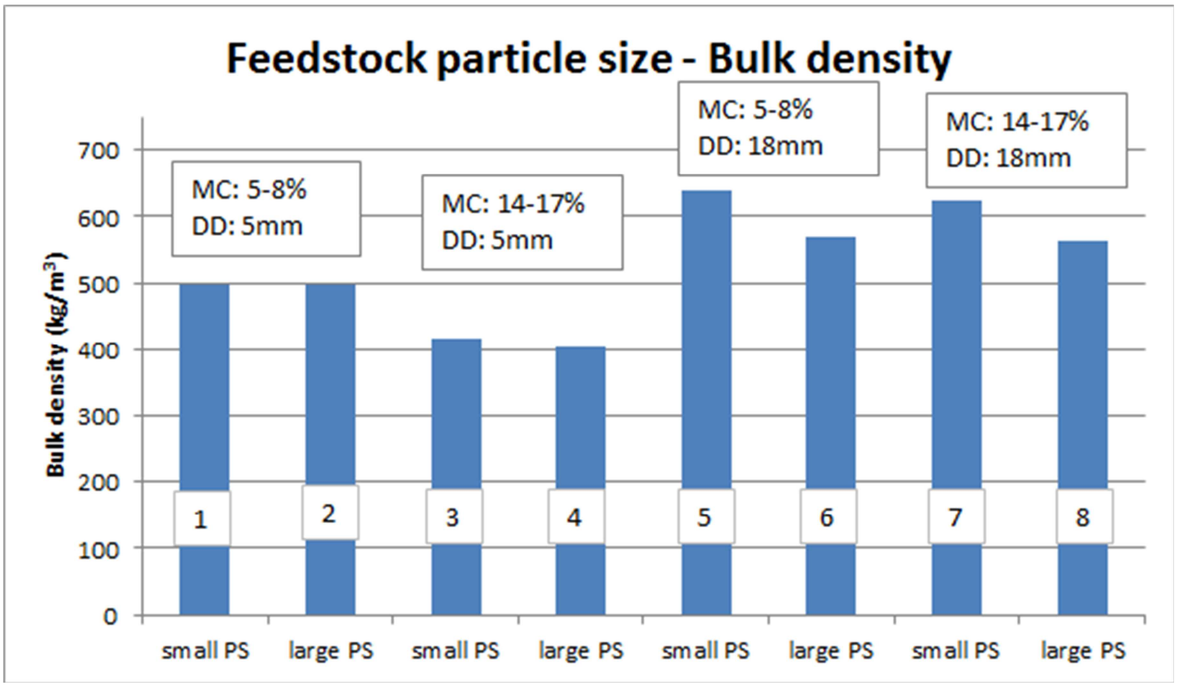

Figure 5.28: The effect of feedstock particle size on the bulk density

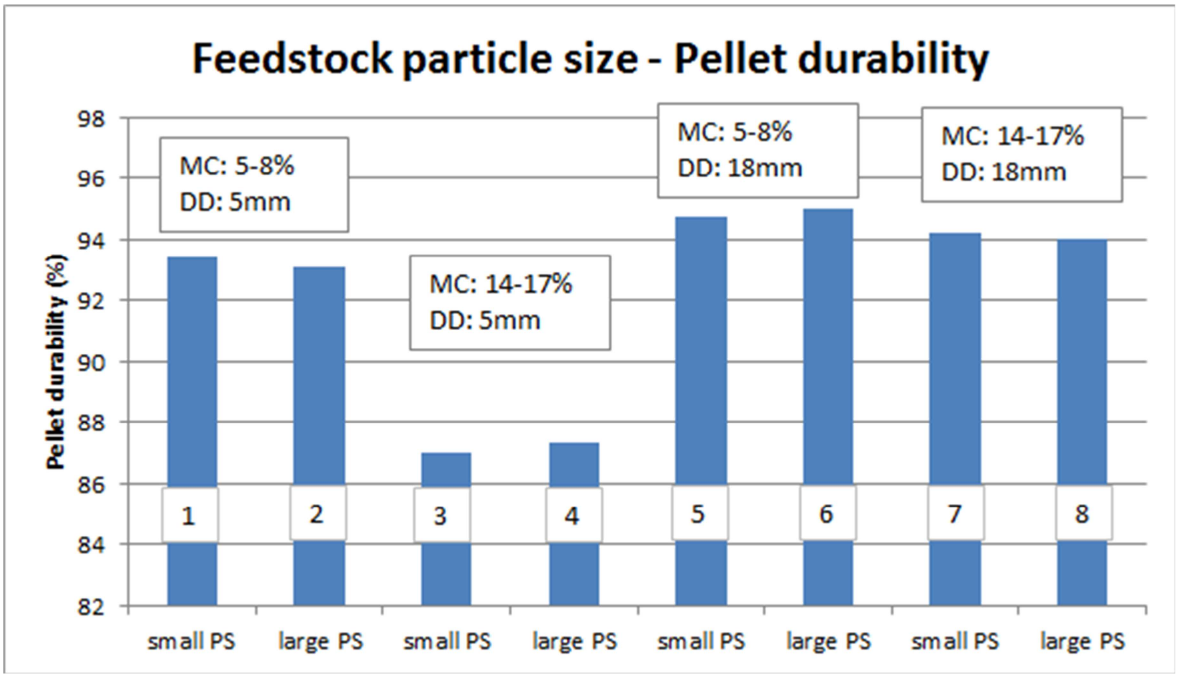

Figure 5.29: The effect of feedstock particle size on the pellet durability

5.4.3 Effect of die diameter on pellet quality

The effect of the die diameter on the pellet quality is shown in Figure 5.30. In each case the use of the 18 mm die diameter increased the density of the pellets. The reason for this effect could be the higher current that was required and used by the larger diameter die as discussed in previous sections (Figures 5.15 and 5.18), which led to higher pressures from the pellet mill on the feed and in turn, leading to increased densities.

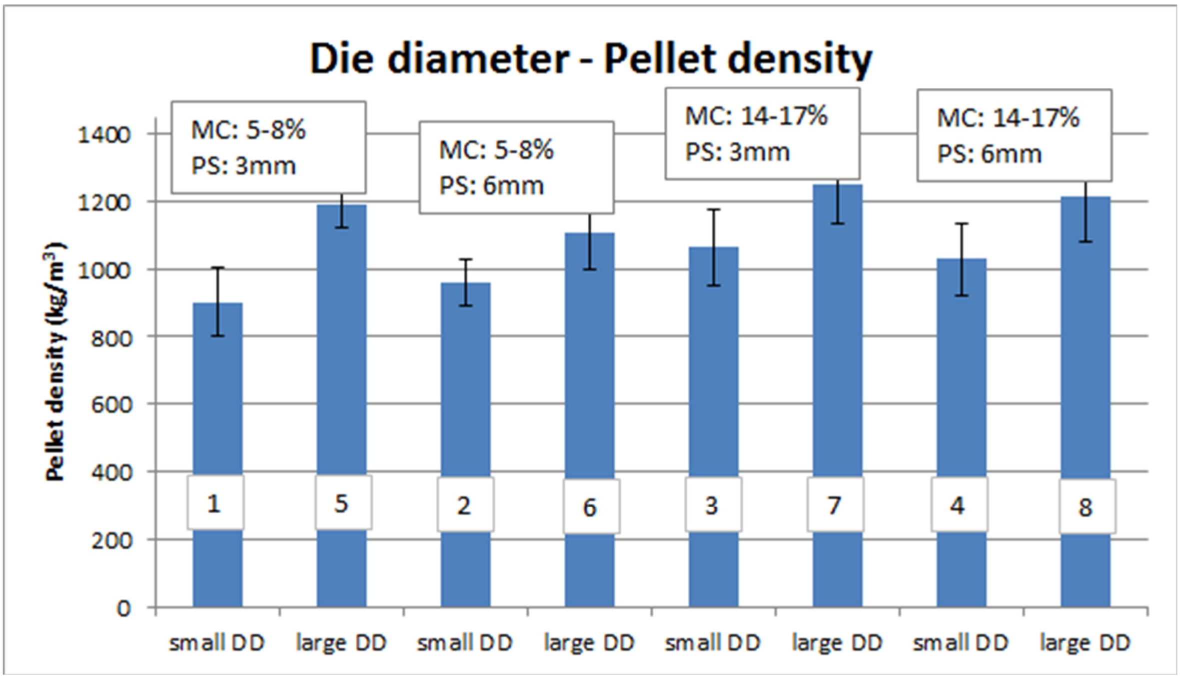

Figure 5.30: The effect of die diameter on the pellet density

The diameter of the die was observed to have an effect on the bulk density of the pellets where the 18 mm diameter die resulted in an increased bulk density. This is illustrated in Figure 5.31. Although it is logical that material of smaller size would have higher bulk density, this was not the case as the pellet density wasn't the same among the pellets. The higher pellet density, which was a result of using the 18 mm diameter die, led to a higher bulk density of pellets. Simply speaking, the large pellets were heavier in a specific amount of volume in comparison to the small pellets.

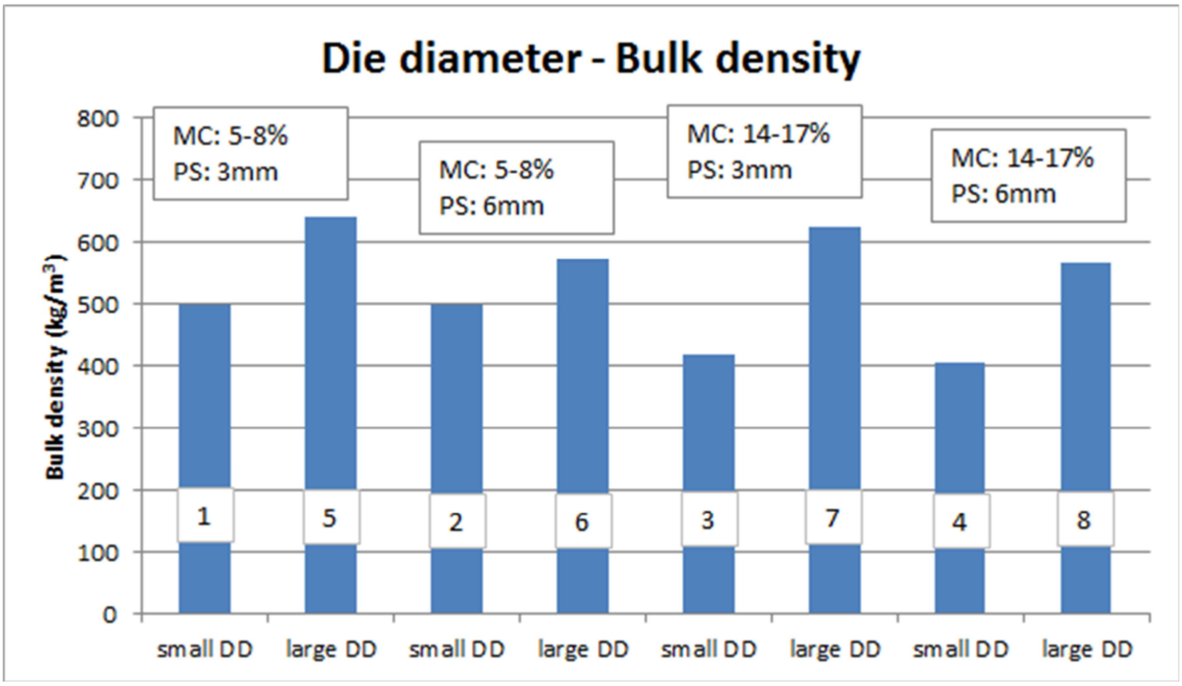

Figure 5.31: The effect of die diameter on the bulk density

The diameter of the die was observed to have an effect on the pellet durability where the 18 mm diameter resulted in an increase of the pellet durability. This is highlighted in Figure 5.32. The reason for the higher durability was the increased temperatures observed during the utilization of the 18 mm die; a direct effect of the high current used. The increased temperature led to a higher flow of the inherent binders of the feed such as lignin, and in turn contributed to an increased pellet durability. The phenomenon was more apparent in the pairs “3,7” and “4,8” due to the higher moisture content and its evaporation during the tests 7 and 8.

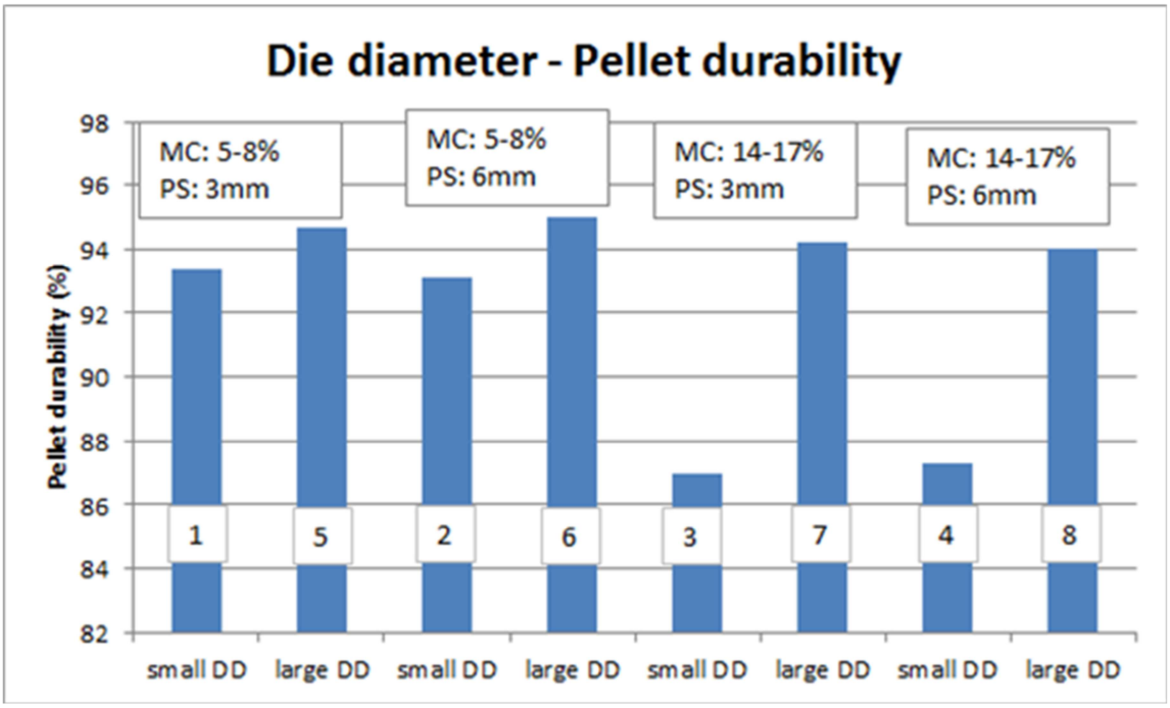

Figure 5.32: The effect of die diameter on pellet durability

5.5 General discussion on the pelleting process

The parameters examined in this study, the feedstock moisture content, the feedstock particle size and the die diameter, have an impact on the pelleting process and pellet quality. A summary of this impact is shown in Table 5.3. The assessment was done through the investigation of two very important parameters that can be exhibited from the pelleting process. These two parameters are the current that was dissipated by the pellet mill in order to process each specific material (measured in amps) and the level that the temperature of the die have reached during the process.

Initially the study highlighted the effect that the feedstock and initial pelleting parameters have on the pelleting process. In the case of the effect of moisture content on the pelleting process it was found that the increased moisture content decreased the amount of energy that the pellet mill required in order to process the material. The reason for this was that the moisture acted as a lubricant, curtailing the friction between the feed and the die-hole surface during the extrusion. This is in agreement with a past study into this effect [57].

Table 5.3: A summary of all parameters and relationships examined for the pelleting process

Figure	Parameter X	Parameter Y	5mm die relationship	18mm die relationship	Possible explanation
5.11	MC	Amps	negative	negative	Moisture acts as a lubricant
5.12	MC	Die temp	negative	negative	
5.13	PS	Amps	positive	no effect	Further size reduction of chop in 5mm die
5.14	PS	Die temp	positive	no effect	
5.15	DD	Amps	positive		Higher friction due to longer die holes
5.16	DD	Die temp	positive		
5.18	Amps	Pellet density	negative	negative	Extra current required due to absence of moisture
5.19	Die temp	Pellet density	negative	negative	
5.20	Amps	Bulk density	Positive (rapid)	Positive (mild)	
5.21	Die temp	Bulk density	Positive (rapid)	Positive (mild)	
5.22	Amps	Durability	Positive (rapid)	Positive (mild)	Higher current lead to higher temp that lead to activation of natural binders
5.23	Die temp	Durability	Positive (rapid)	Positive (mild)	
5.24	MC	Pellet density	Positive	Positive	Moisture acts as binder
5.25	MC	Bulk density	Negative	Not apparent	
5.26	MC	Durability	Negative (sharp)	Negative (mild)	Higher moisture lead to higher spaces between the chopped particles
5.27	PS	Pellet density	Not clear	Negative	Smaller particles occupy empty space
5.28	PS	Bulk density	No effect	Negative	Due to pellet density
5.29	PS	Durability	No effect	No effect	
5.30	DD	Pellet density	Positive		Higher current, higher pressure
5.31	DD	Bulk density	Positive		Higher pellet dens, higher bulk dens
5.32	DD	Durability	Positive		Increased temp in 18mm die, higher flow of natural binders

The feedstock particle size, either the 3 mm or the 6 mm, did not have any visible effect upon the pelleting process when using the 18 mm die. However, the 6 mm particle size has an effect during the utilization of the 5 mm die by increasing the current required by the pellet mill. The extra current was used by the pellet mill for further size reduction of the feedstock. The size reduction takes place in the space between the rollers and the die holes, due to the larger size of the feedstock in comparison to the die diameter. The effect was also projected on the temperature that generally increases during further size reduction within the die.

The die diameter has also a significant impact on the pelleting process. The 18 mm die diameters are responsible for the increase in the friction between the feed and the surface of the holes due to the higher accumulation of feed inside the holes and the greater length of the die holes. The pellet mill tries to overcome the friction by using larger amounts of energy and thus the temperature also increases. Similar results were reported by Heffner *et al* [102]. Furthermore Pfost [103] reported that the decrease in the die length leads to reduced energy requirements by 37%.

In Figures 5.18 and 5.19, the relationships are shown between the current used by the pellet mill and the density of the pellets and furthermore the relation between the temperature of the die and the density of the pellets. It was shown that the wet feed yielded the higher pellet density and also required less energy by the pellet mill.

However, the dry feed had lower pellet densities and due to the lack of moisture, higher amounts of energy were required by the pellet mill to complete the process due to the higher friction between the particles themselves and the friction between the feed and the surface of the die holes.

Gilbert *et al* [104] observed an increase of the pellet density with an increase of the pressure. Similarly, Mani *et al* [46] reported the increase of pellet density with an increasing compressive force for four different biomass samples. In this study differences were observed due to the fact that the current was affected greatly by the lack of moisture.

The bulk density also has a relationship with the electric current and the temperature. It is shown that whenever the process leads to an increase of the energy required by the pellet mill, the bulk density also increases. Similarly this trend is observed between bulk density and temperature.

In addition, it is shown that the increase of current will result in a higher durability of the pellets due to the activation of the natural binders that occur in the process due to the higher current used leading to higher friction, in turn leading to higher die temperatures. This is in agreement with results reported by Tabil *et al* [52, 105], in which increased energy consumption is connected with a rise of the durability.

Importantly this study shows the effect of the pelleting parameters prior the pelleting process upon the quality of the pellets. The increase of moisture content leads, to a point, to an increase of the pellet density by means of the binding characteristics of moisture (capillary and interfacial forces [53]). Ryu *et al* [51] reported an increase of pellet density due to an increase in moisture content. However, Sokhansanj *et al* [61] reported a decrease of pellet density with an increase of moisture. Furthermore, Gustafson and Kjelgaard [106] also reported a decrease of pellet density with an increase of moisture content. Similar results also reported by Mani *et al* [46]. Lehtikangas [56] reported that moisture exhibits a binding behaviour in pellet production. The differences in the trends found in literature are possibly happening due to the measurement of moisture content in the feedstock and the pellets.

Moisture content also impacts the bulk density, but the effect is most apparent in the 5 mm diameter pellets. A negative trend between the moisture content and the bulk density was also reported by other authors [59]. Sokhansanj [61] reported an increase of the bulk density, up to a point, and then a constant decrease of bulk density with an increase of moisture content.

The moisture has an influence on the durability, however this trend is negative. The tests on the pellets show that an increase of the feedstock moisture content decreases the pellet durability. This is because the increased moisture leads to higher spaces between the chopped particles due to the incompressibility of the water. On the other hand, too low moisture content could lead to a significant increase of the friction forces between the particles and the die that could result in the formation of fire or smoke which amongst other issues, compromising the fuel property of the final pellet. Too low moisture content could also lead to the blocking of the die. The optimum feedstock moisture content would be between 8 and 14%. The trend between the moisture content and the pellet durability has been reported elsewhere however the bulk of the literature shows an increase of the durability with increasing moisture due to the fact that the studies are mostly within the range of 8 – 15%. Larsson *et al* [59] reports an increase of the durability with increasing moisture content up to 15%. Smith *et al* [107, 57] showed that the durability increased with an increase of the moisture content from 10 to 15%. The same trend was shown also by Kaliyan and Morey [108, 57] for the same range of moisture content (10-15%). Increasing the moisture content even further, the durability decreases as was shown by O'Dogherty *et al* [109, 57] where the authors increased the moisture content from 20 to 35%. In addition, Lehtikangas [56] reported the positive correlation between the moisture content and the durability only up to a point. The decrease of the durability (increased abrasion) with a rise in the moisture content was also reported in [110].

The particle size does not have a clear effect on the density of the small size pellets because the 6 mm feedstock particle size was larger than the die holes and thus, further size reduction occurred inside the die. On the other hand it does have an effect on the 18 mm diameter pellets. It was shown that the 3 mm particle size tends to increase the pellet density due to the occupation of the empty spaces from the particles. The 6 mm particles led to a decrease of the pellet density because a greater number of empty spaces exist within the pellets. Furthermore the 3 mm size feedstock has a larger total particle surface and thus the binding behaviour of moisture is more functional with the small rather than with the large feedstock. The increase of the pellet density by the utilization of finer particle size chop was shown by Dobie [111, 47].

The 6 mm particle also has an effect on the bulk density of the 18 mm pellets. The bulk density was found to be smaller with the large chop in comparison to the pellets manufactured by the 3 mm feedstock. This is possible due to the decrease of the pellet density with an increase of the particle size as described before. Furthermore Mani *et al* [46] reported that the feedstock that was made by using the larger screen, it also had the lowest bulk density (as a chop). Possibly the latter was another reason for the decreased bulk density with an increasing feedstock particle size. Similar results were reported for the chop by Lam *et al* [112], the larger the particle size, the smaller is the bulk density of the chop. Thus it is possible that the small bulk density of the chop results in pellets with also a small bulk density.

Concerning the durability, it was found that the particle size did not affect this property. The results of the current study do not agree with the findings of Hill and Pulkinen [113, 47] who reported a 15% increase of the pellet durability with a decrease of the screen size. The results also don't agree with findings reported by Singh and Kashyap [114, 57] that the decreasing particle size of rice husks increased the durability of the briquettes from 84.1 to 95%. It is possible that the previous authors used a wider range of particle sizes so an affect could be observed. Other results though, taken from the literature, do agree with the results of the current study such as those pointed out by Briggs *et al* [58] that the particle size did not have any considerable effect on the pellet durability. Likewise Tabil and Sokhansanj [105] reported that the different hammer mill screen sizes didn't cause any significant differences in the durability.

In the case of the die diameter it was observed that it positively affected all the properties under investigation. The pellet density of the 18 mm pellets was higher in comparison to the one of the 5 mm pellets because the 18 mm die has longer holes that needed higher electric current and thus higher pressure in order for the feed to pass through, however, the use of the

18 mm diameter die caused many problems to the process due to the high temperatures that were exhibited and the general absence of lubricants

Because of the higher pellet density, the bulk density of the 18 mm pellets was also higher than the one of the 5 mm pellets. The results, agree with the ones of Lehtikangas [56] that reported that the pellet density has a positive effect on the bulk density.

Concerning the durability, due to the higher current, higher die temperatures were achieved leading to increase of the flow of the natural binders of the feed such as the lignin and thus to increase the durability. Similar results reported by Heffner and Pfost [102]. Tabil and Sokhansanj [105] reported a better pellet durability with an increased l/d ratio with the effect being more pronounced in the case of the large diameter dies.

5.6 Problems and suggestions for the pelleting process

During the course of this study, a large sample of the manufactured pellets that described in the previous sections was supposed to be manufactured within the Cranfield University. The University has in its possession a pelleting unit that was described in chapter 4 “Experimental Procedure”. Unfortunately the pelleting unit did not function as expected and that was the reason that the oilseed rape straw pellets were manufactured elsewhere.

The design problems that were identified concern issues along all the range of the pelleting unit: from the efficient functioning of the hammer mill and the transport of the material from the hammer mill to the pellet mill to the design of the die and the mechanism of addition of water and oil. Although many of the problems were solved with certain small alterations in the design of the rig, the manufacturing of the pellets with the necessary properties was not possible. Pellets could be produced but the pellet mill had lots of difficulties to do that without the addition of binder and oil.

The pellet mills with hollow perforated dies and feed from the inside is one of the most common pellet mills in the market (Cranfield pellet mill is of this type). A typical design of this kind of pellet mill with the perforated die and two rollers can be seen in Figure 5.33. Due to the fact that the die cannot be very wide for structural reasons, the capacity of the pellet mill can be increased by installing more rollers. Two rollers can double the capacity in comparison to one roller and three rollers can triple it [110, 115]. The Cranfield pelleting unit is already equipped with two rollers and thus not further rollers are required.

Figure 5.33: A typical interior of a ring die [115]

The original plan dictated the use of extreme values for the concerning properties; big die, small die or high moisture content, low moisture content etc. That was the reason for the initial choice of 4 mm and 15 mm pellet die (Cranfield pelletiser). The l/d ratio (length over diameter ratio) of these to dies is shown in the Table 5.4. In the current section, certain suggestions for the general pelleting process and also, more specifically, for the Cranfield pelletiser, are discussed.

Table 5.4: Die size and length to diameter ratio

Die size (diameter)	**l/d ratio**
4mm	8.25
15mm	6.3

The major parameters that affect the compression efficiency during the pelleting process are the friction characteristics of the die, the dimensions of the hole, the size and dimensions of the material that forced into the hole, the rolling velocity, the material and shape of the die and the rolls and the compression capacity of the pellet mill [49].

The extrusion ratio (or compression ratio or press ratio), as described previously, is the ratio of the length of the die over the diameter of the die and it determines the level of friction to be applied inside the compression channels. Higher extrusion ratios (larger die lengths) can be used whenever the material does not include natural binders, e.g. small amounts of lignin. The increased extrusion ratio will result in higher temperatures inside the die and it would be possible for the natural binders to flow easier but only up to a point [110].

Straw is a difficult material to pelletise and thicker dies (longer holes) should be used. In order to pelletise wood a common practise is to use extrusion ratios of 3/1 to 5/1 but for straw it's necessary to use 8/1 in order to increase the friction, the temperature and to ease the flow of the lignin. Furthermore another disadvantage of straw in general is the increased silica content that tends to wear the dies faster in comparison to wood [49].

Higher densification can be accomplished with the increase of the length/diameter ratio. Furthermore in order for the pelletisation process to be successful the extrusion force must be larger than the frictional resistance, thus the die thickness should be selected as such not to break during the operation [115]. The densification process within the pellet mill depends on the friction between the surface of the compression channel and the material which in its turn depends highly on the moisture content. That is why optimum moisture content value is required which is usually between 8 and 12%. In the case that the material is pre-treated using steam then the moisture content of the feeds should be slightly less than the optimum so that would compensate for the added water [110].

The type of material is very influential on the pelleting process. Basically, it is the pellet mill that has to be adapted to the feedstock properties and not vice versa. That is why pellet mills that are used to process a specific material, cannot efficiently process another type of material. Possible alterations in the die could be on the thickness of the die, the length of the compression channels, the quantity, shape and dimensions of the holes, the number, diameter, shape and type of the rollers [110].

Conditioning is in general the addition of small amounts of lubricants or the addition of steam to heat, moisten and in certain cases to gelatinize starchy material or to soften the material by heat addition. Heat can be added through the steam but extra heat is also generated during the extrusion process. The extra heat is easily removed with the cooling process after the pelletisation [115].

As explained, the herbaceous biomass is in general a difficult material to be pelletised because of a lower amount of natural binders and the intensely fibrous nature. Except alterations in the specifications of the die, different binding agents could be added in order to ensure the improved binding characteristics of the material. Additive such as molasses, lignosulphonates, starch, lime or even sawdust could improve the results. The mixture of the herbaceous biomass with woody biomass would also overcome few problems. Furthermore special techniques such as the defibration could be used to ensure higher quality of pellets

[110]. Investigation on the additives that could be possibly fit to the pelleting of oilseed rape straw or other types of herbaceous biomass would be imperative to the operation of the Cranfield pelleting unit.

Steam is a very important additive to the pelleting process. The additive steam should be slightly superheated so that would not have any excessive increase of the moisture content of the feed. Steam conditioning contributes to the reduction of wearing of the die and to the increase of quality of pellets. Steam is also characterized by its lubricant characteristics and thus the reduction of excessive friction between the surface of the die hole and the material that leads to increased efficiency and decrease of the wearing of the die. The biggest advantage of steam conditioning is that it activates the lignin in order to flow easier and makes the material more malleable and thus the binding strength of the fuel increases. During the cooling process moisture content is decreased so that might compensate for the extra moisture added during the steam conditioning [49]. Addition of steam during the utilization of the Cranfield pelletiser should be highly considered as a priority.

Additives are not only used to increase the density or the durability of pellets but it can also be used to improve the chemical characteristics of the pellets to achieve higher efficiency in the thermal conversion process. Slagging for example can be reduced with the addition of kaolin or calcium and magnesium oxides [49].

One of the observations made during this study, and is applied to all the pelletisers, was that the large particle size is further reduced inside the pelletiser while a small diameter die is used. It is typical that in a 6 mm die the chop size should be around 4 mm. In order to grind the feedstock even further would require higher input energies [110].

In general very fine particle sizes are more cohesive in nature and their chop bulk density is low (high bulk volume). Because of that, the collapse of the cohesive arches (internal binding arches that board a large quantity of gas) due to the escape of a large amount of air, occurs. What remains between the fine particles are small pores filled with gas that cannot easily escape due to the low diffusivity, and thus longer time is required for a large amount of gas to escape. The degassing and deaeration problems are usually solved by using a force feeder so that the initial chop bulk density will increase [115]. The pelleting unit of Alchemy Technology (manufacturer the OSRS pellets) is equipped with a force feeder. As a final solution, a force feeder should be considered for the Cranfield pelleting unit, although the problem could be partially solved by using larger than 4 mm particle size feedstock, however it would be difficult to use the 4 mm die.

The distance between the die and the rollers also plays a role in the performance of the pellet mill. The feed is inserted into the spinning die and it is distributed evenly all along the internal surface of the die. When the thickness of the feed layer on the surface of the die reaches a particular value the rollers start rotating too. In time, the compression of the rollers upon the feed increases and whatever feed was staying at the edge of the compression channels (holes) is forced to get through and thus the extrusion process starts [110]. With the increase of the distance from 0 to 1mm, it was observed the increase of the energy demand but at the same time it was also observed a reduction of the amount of fines by 30%. This could be a solution to one of the problems encountered with the Cranfield pelletiser. The cranfield pelletiser was producing a high quantity of fines so by increasing the distance between the die and the roller, the amount of fines will be reduced. At this stage a new problem was found. A design problem was the inability to adjust that space between the die and the rollers even though there is the capability on doing that. The shaft of each one of the rollers has 6 holes which exist for the sole reason of adjusting that space. The pelletiser functions at the 6th and final hole. The space cannot be increased because there are no more holes and cannot be decreased it either because the placement of the roller to the 5th hole results in the touching of the die and the roller. So there is imperative need for a more flexible system of space adjustment [49].

The shape of the compression channel (see Figure 5.34) also plays a role in the quality of the pellets produced. The simplest of the shapes is ‘a’ and represents a compression channel with chamfered inlet to compensate for the large space between the inlets of the holes. The chamfer helps to guide the feed into the compression chamber. Due to the fact that some dies should be thick (long), the compression channel is also long but to compensate for the high frictional resistance shapes ‘b’, ‘c’ and ‘d’ may be used. In that way the length of the compression channel decreases by increasing the size either of the inlet or of the exit. In general during the pelleting process, if the elastic deformation does not permanently change into plastic deformation then the pellets expand at the exit of the compression channel. If the exit of the channel has sharp edges(such as in the Cranfield pelletiser), the expansion is sudden and that results in the cracking of the surface of the pellets taking the shape of “Christmas tree”. The latter effect could be formed even in compression channels such as the one shown in shape ‘d’ which include a relieve bore. In order to avoid the cracking during the pellet expansion (swelling), the exit of the compression channel could be tapered such as in shape ‘e’. The swelling is caused by the expansion (elastic spring-back) of the compressed residual air that exists inside the pores of the pellets and the relaxation of elastic deformation [115]. Finally the shape ‘f’ represents a channel with chamfered inlet, tapered exit and relieve bore that could be a good solution when even when properties in the extreme ranges are used [115].

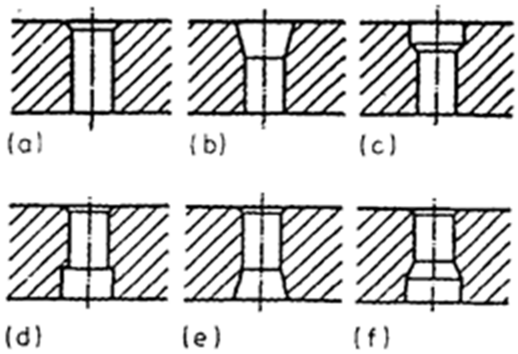

Figure 5.34: Six different types of compression channels in a die [115]

The tapered exit and the relieve bore in ‘f’ make the counter-bore. The main bore is used to decrease the length of the channel and the tapered exit is used to achieve a gradual elastic expansion. Tapered inlet is used for two main reasons. The first reason is to increase the opening area without sacrificing the strength of the main body of the die. The latter effect usually occurs during the pelleting of fibrous material, such as straw, that can produce matting and clog the die if large space exists between the holes. The second reason to use tapered inlet is to obtain additional compression and that could be used with feeds that have low bulk density, such as the feeds made of small particle chop [115]. The Cranfield pelletiser uses dies of type ‘a’. Possible alterations to type ‘e’ or ‘f’ would increase the quality of the performance of the pelletiser. If a die wears off, replaceable parts can be used in certain occasions. An alternative solution, in the case of Cranfield pelletiser, replaceable parts could possibly be used in the large diameter die (15 mm) to convert it from an ‘a’ type to ‘e’ or ‘f’. The consequences would be the decrease of the diameter of the compression channel and the increase of the l/d ratio (from 6.3 to possibly more than 8) but this could be compensated by the tapered inlet and exit and the relieve bore.

Other problems can also appear during the pelleting process such as the die blocking which can be overcome using a by-pass chute [49]. Another usual problem during the pelleting process is the density variations within the pellets. This may lead to cracks and to a decreased quality of the pellets. The compression force is a direct result of the friction between the surface of the compression channel (holes of the die) and the material. This may result in pellets that the outer pellet surface has higher density in comparison to the inner part of the pellet. The density variations are the direct result of the interparticle and wall friction, the dissipation of force from particle to particle and the shear forces between the particles. Density variations can increase with higher compression force and with longer pellets. It may decrease with the increasing diameter (even with the same l/d ratio), the addition of a lubricant and the lubrication of the die walls (such as with steam conditioning) [115].

A difficult situation that might appear during the pelleting process is the overfeeding. In the normal case, the material forms a layer between the main body of the die and the rollers. The sufficient thickness of that layer causes the rollers to rotate, entrain and compress the layer along the main body of the die. At that moment the holes on the main die body are fed with material while the rollers are rotating and keep entraining and pressing the feed layer towards the die body and the die holes. In the case that the layer of material is too thick, the rollers meet the material, while rotating, at their sides, an upward force is pushing the material to form a cyclic motion right at the meeting point between the layer and the roller. At that point the material accumulates and thus it cannot be entrained [115].

In this chapter an overview of the pelleting process was presented. Firstly, the manufacturing method and the problems occurred during the pelleting process was discussed. This was followed by the effect of the pelleting parameters (feedstock moisture content, particle size and die diameter) on the pelleting performance (represented by the amps of the pellet mill and the die temperature). A relationship was established between the pelleting performance and the quality of the pellets (represented by the pellet and bulk densities and the pellet durability). The latter was followed by a discussion on the effect of the initial pelleting parameters on the pellet quality. Suggestions were made to improve the performance of the Cranfield pelletiser. The effect of the pelleting process on the gasification process will be discussed in the next chapter.

6 The gasification process

In this chapter, the results and discussion of the gasification process are going to be presented starting with the analysis of the downdraft gasification process, using oilseed rape straw pellets as a feed, which will be followed by the results of the spouted fluidised bed gasification process using the same feed. Furthermore, results are presented of gasification processes using other material such as Miscanthus and DDGS pellets. Finally, the gasification outputs will be related with the pellet quality characteristics and ultimately with the initial pelleting parameters.

6.1 The downdraft gasification of oilseed rape straw pellets

The downdraft gasification tests were conducted in the pilot scale rig as discussed in the "experimental procedure" chapter. The feed of the downdraft gasifier was performed in batches and not continuously and this means that the material feed-rate is directly affected by the air feed-rate and the type of the pellets. Representative graphs and tables of the temperature profiles, gaseous species and gasification performances are presented.

6.1.1 Downdraft gasification of 5 mm OSR straw pellets

The comparison of the performances of the different pellets was done keeping the same or similar equivalence ratio which is shown in the performance tables. The performance tables also include the process parameters which are the biomass or pellet feed rate and the air feed rate, the gas composition including all the major gasification species such as the CO, CO_2, H_2 and CH_4. The mass balance was calculated using the nitrogen balance equations as explained in section 4.4 The performance quality assessment is completed using certain parameters such as the higher heating value (HHV), the cold gas efficiency, the carbon conversion efficiency, CO/CO_2 ratio, the mass conversion factor, the specific energy rate and the gasification rate which were all explained in section 4.4. The results in bold (in the Tables) are those test results that are used later on to compare the pellets between them.

In the Table 6.1 it can be seen the performance of the 5 mm oilseed rape straw pellets within the range of 0.3-0.35 of equivalence ratio (ER). The CO production is within the range of 9-

12% while the HHV doesn't exceed the 3.2 MJ/m^3. Carbon conversion reach the range of 50-60% while the cold gas efficiency is within the range of 20-35%. The amount of the hydrocarbons converted is between 0.38-0.55 as it is shown by the mass conversion factor. Furthermore, the specific energy rate and the gasification rate reach a little more than 1100 MJ/m^2*h and 80 kg/m^2*h respectively.

Table 6.1: Performance of the 5 mm oilseed rape straw pellets in a downdraft gasifier within the ER range: 0.3-0.35

		OSRS pellet type					
		1	2	**2**	2	**3**	**4**
Biomass feed (kg/h)		7.6	7.6	7.6	7.8	7.3	7.2
Air feed (l/min)$^{(1)}$		230$^{(1)}$	210$^{(2)}$	240$^{(3)}$	240$^{(3)}$	200$^{(4)}$	200$^{(4)}$
Equivalence ratio		0.33	0.3	0.35	0.35	0.33	0.33
Average gas composition	CO	11.34	12.3	11.1	11.15	8.9	9.2
	CO_2	15.1	14.8	15.2	14.9	15.8	15.8
	H_2	8.3	9.3	8.5	7.95	6.44	5.7
	CH_4	1.14	1.18	1	0.97	0.9	1
	N_2	64.12	62.51	64.2	65.03	67.96	68.3
Gas yield ($m^3/kg_{biomass}$)		2.25	2.1	2.34	2.25	1.92	1.94
HHV (MJ/m^3)		2.94	3.2	2.88	2.8	2.3	2.29
Cold gas efficiency (%)		34.6	35	35	33	23	23
Carbon conversion efficiency (%)		59.3	57	61	58	50	51
CO/CO_2 ratio		0.75	0.83	0.73	0.75	0.563	0.582
Mass conversion factor		0.53	0.53	0.545	0.5	0.38	0.385
Specific energy rate (MJ/m^2*h)		1111	1136	1135	1091	714	705
Gasification rate (kg/m^2*h)		80	80	82	78	54.9	55

(1)Error: <5%, ±11.5 l/min
(2)Error: <5%, ±10.5 l/min
(3)Error: <5%, ±12 l/min
(4)Error: <5%, ±10 l/min

A disadvantage observed during the oilseed rape straw gasification was the general poor performance concerning the CO production as it is shown by the CO/CO_2 ratio which is always remains below 1. A detailed comparison between pellets and the reasons that led to this performance are discussed in the following paragraphs.

The Figures 6.1-6.6 represent a sample of the downdraft gasification of the 5 mm oilseed rape straw pellets.

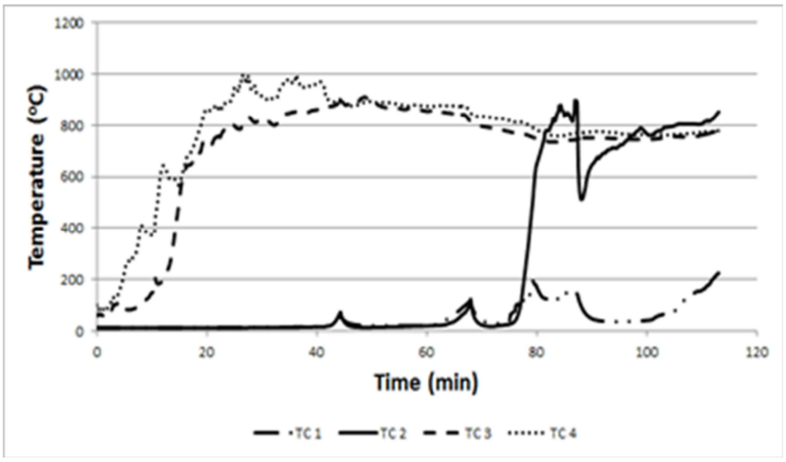

Figure 6.1: OSRS pellets type 1 temperature profile

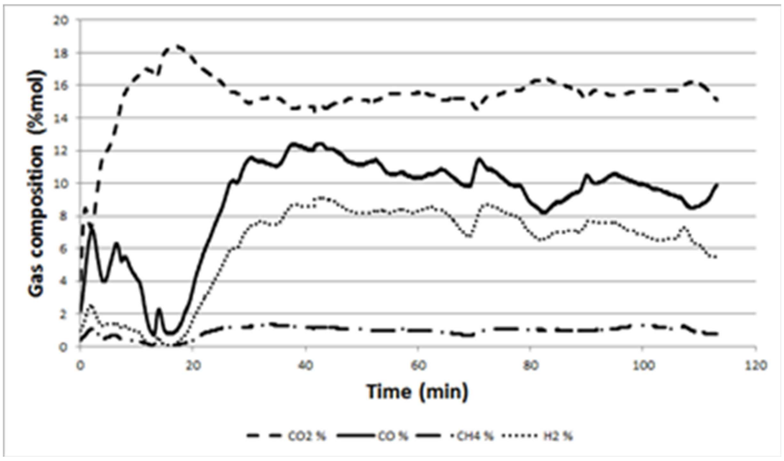

Figure 6.2: OSRS pellets type 1 gas composition

Figures 6.1 and 6.2 show the online temperature profile and the gas composition of the type 1 (MC: 5-8%, PS: 3 mm and DD: 5 mm) pellets respectively, as they were gasified in a downdraft rig. Similarly, the Figures 6.3-6.6 show the temperature profiles and gas compositions for the types of pellets 2 (MC: 5-8%, PS: 6 mm and DD: 5 mm) and 3 (MC: 14-17%, PS: 3 mm and DD: 5 mm).

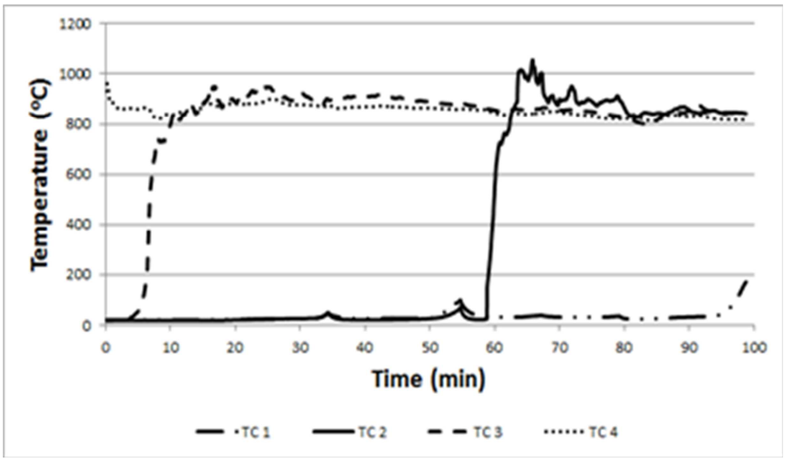

Figure 6.3: OSRS pellets type 2 temperature profile

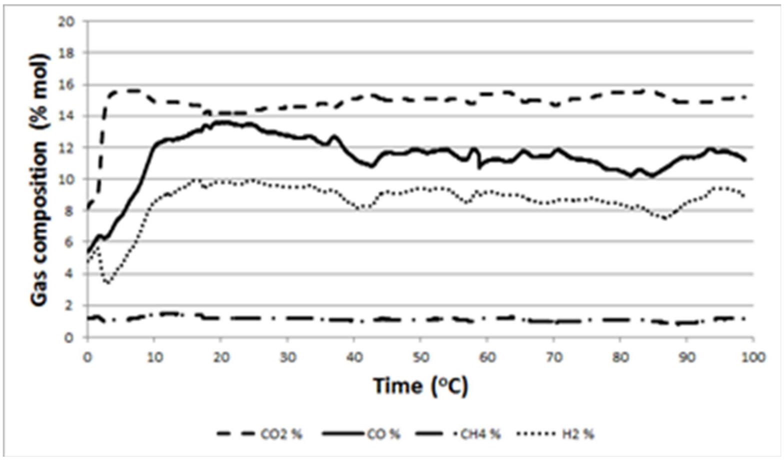

Figure 6.4: OSRS pellets type 2 gas composition

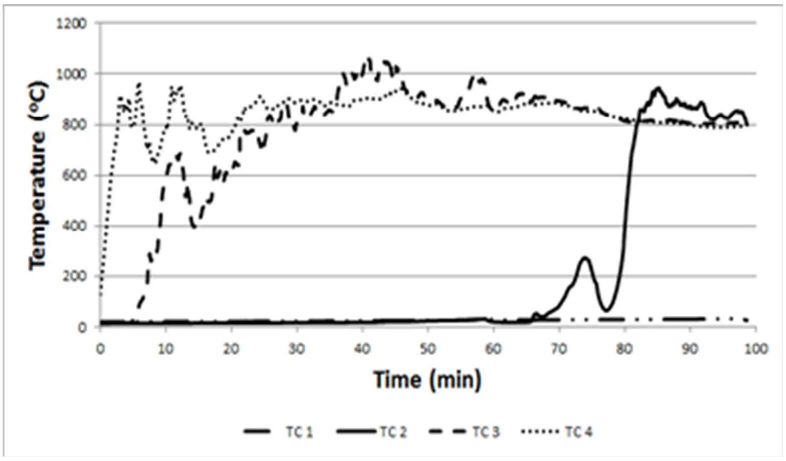

Figure 6.5: OSRS pellets type 3 temperature profile

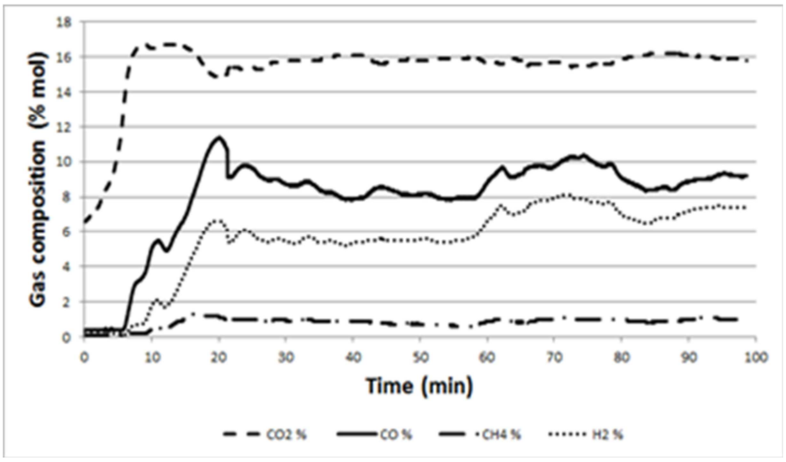

Figure 6.6: OSRS pellets type 3 gas composition

As it can be seen from the Figures 6.1-6.6, the temperature during the tests remained relatively constant at around 800°C. The temperature plays a major role in the gasification process and great efforts were made to ensure consistency in every test. However, due to the self-sustaining nature of the gasification process, the temperature was always affected by numerous parameters such as the air feed rate and the type of the pellet, pellet size, amount of ash and quality and bed agglomerates. Thus, keeping the equivalence ratio similar and without providing any continuous external heat source, the comparison between the pellets actually demonstrate if the temperature was affected by the pelleting parameters. Although it is expected that there is a relation between the pellet type and gasification performance it is not easy to quantify this relation. Including the fact that gasification performances always have differences between them even when consistent process parameters are used, the temperature does not escape this general rule and differences are observed in the temperature between the tests even when the same process parameters are used. Thus the differences in temperature will be mentioned in this project, and they will be treated mostly as direct influence of the gasification quality as well as effect of the process parameters.

6.1.2 Downdraft gasification of 18 mm OSR straw pellets

There was a number of practical issues in gasifying these pellets and the actual results can be seen in Table 6.2. The extremely low production of combustible gaseous species and the really high production of CO_2 is evident in the experiments. The equivalence ratio (ER) could not be kept constant due to the effort that was made in order to find a successful method of gasifying this material. A range of air feed rates was used from 70 to 240 l/min but without success. In all the tests, the production of CO does not exceed the 1%mol and the amount of

CO_2 never falls below the 16%mol. Similarly, the other combustible gaseous products such as the H_2 and the CH_4 have very low percentages. Consequently, all the performance parameters such as HHV, cold gas efficiency, mass conversion factor, specific energy rate, gasification rate and the CO/CO_2 ratio are extremely low. The only performance parameter that is worth mentioning is the carbon conversion efficiency which in certain case reaches 50-60% however the carbon in the fuel, in this case, was converted mostly to CO_2.

Table 6.2: Performance of the 18mm oilseed rape straw pellets in a downdraft gasifier

		OSRS pellet type				
		5	5	**6**	**7**	**8**
Biomass feed (kg/h)		3.8	3.8	3.9	3.5	4.3
Air feed (l/min)		180[(1)]	70[(2)]	240[(3)]	140[(4)]	220[(5)]
Equivalence ratio		0.52	0.2	0.6	0.48	0.61
Average gas composition	CO	0.2	0.2	0.41	0.5	0.23
	CO_2	17.1	16.6	17.3	17.3	17.05
	H_2	0	0	0	0.11	0
	CH_4	0.1	0.1	0.1	0.08	0.08
	N_2	82.6	83.1	82.19	82.01	82.64
Gas yield ($m^3/kg_{biomass}$)		2.73	1.05	3.57	2.32	2.95
HHV (MJ/m^3)		0.065	0.065	0.092	0.109	0.06
Cold gas efficiency (%)		0.9	0.4	1.76	1.3	0.95
Carbon conversion efficiency (%)		45	17	60.1	41.9	51.6
CO/CO_2 ratio		0.0117	0.012	0.024	0.029	0.0135
Mass conversion factor		0.082	0.02	0.14	0.095	0.086
Specific energy rate (MJ/m^2*h)		15	6	28	20	17
Gasification rate (kg/m^2*h)		6	1.4	11	7	7

(1)Error: <5%, ±9 l/min
(2)Error: <5%, ±3.5 l/min
(3)Error: <5%, ±12 l/min
(4)Error: <5%, ±7 l/min
(5)Error: <5%, ±11 l/min

There could be numerous reasons for the failure of the 18 mm pellets to be gasified. A reason could be the inability of the downdraft gasifier to tolerate large fuel sizes. This trait of the downdraft gasification units is generally applied to most of the downdraft gasification rigs and thus it is safe to say that the results could be similar in other downdraft rigs as would be discussed later or at least the difficulty of gasifing these pellets would be recognized.

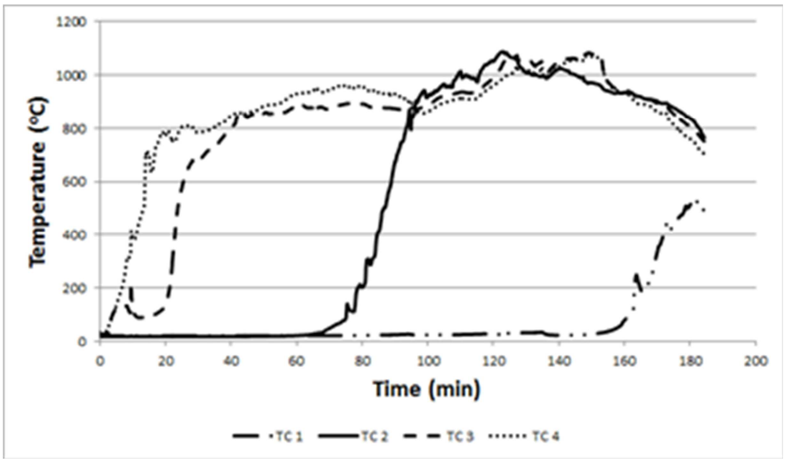

Figure 6.7: OSRS pellets type 5 temperature profile

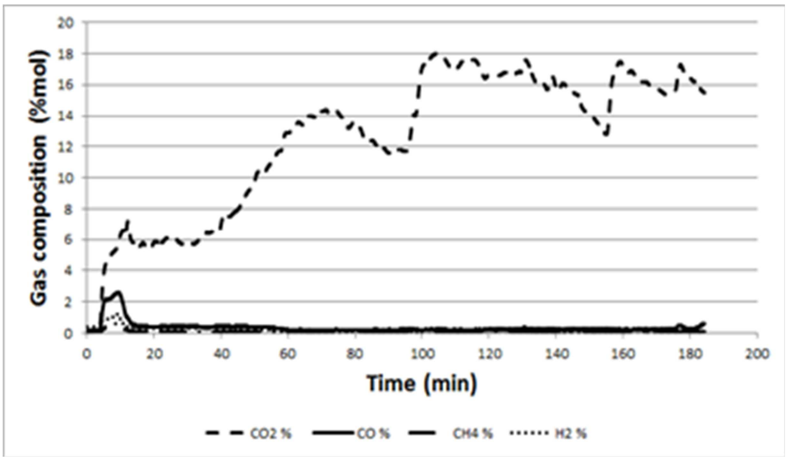

Figure 6.8: OSRS pellets type 5 gas composition

Figures 6.7 and 6.8 show the temperature profile and the online gas composition of the type 5 (MC: 5-8%, PS: 3 mm and DD: 18 mm) oilseed rape straw pellets. The temperature reached, around 900^{o}C, even increasing to over 1000^{o}C. This is evident of the lack of gas production. No heat was dissipated for the gas production and thus the temperature has increased. The gas composition shows that CO_2 reached its maximum values at the highest temperatures indicating that combustion was the major thermal conversion process during these tests. Comparing Figure 6.7 with Figures 6.1, 6.3 and 6.5 (temperatures of the gasification tests of 5 mm pellets) it is observed that the heat transfer rate along the bed was not the issue as the heat transfer rate of the 5 mm pellets and the 18 mm pellets is similar. This is observed by considering thermocouple 2 (TC2) in the graphs which show that the temperature in this region of the bed increased at nearly the same time meaning that the heat transfer rate was similar in all the tests despite the different pellet sizes.

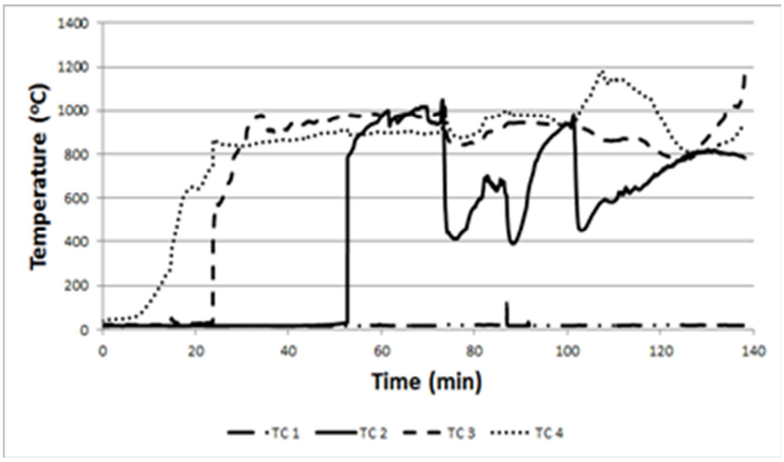

Figure 6.9: OSRS pellets type 7 temperature profile

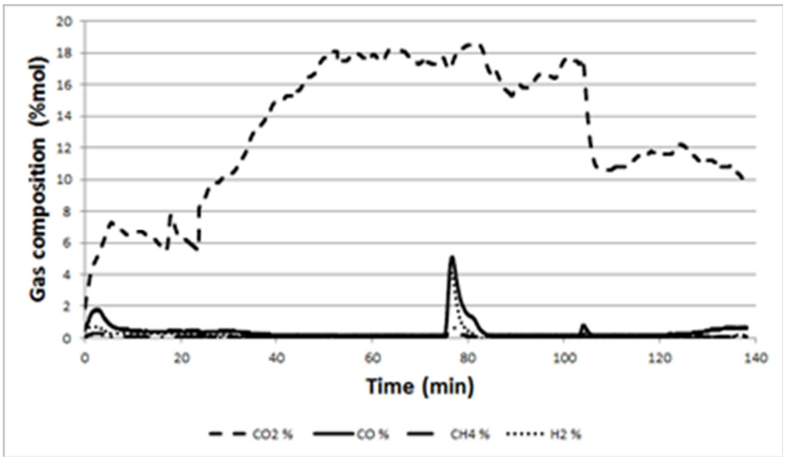

Figure 6.10: OSRS pellets type 7 gas composition

The Figures 6.9 and 6.10 show the temperature profile and the gas composition respectively for the gasification trial of pellet type 7 (MC: 14-17%, PS: 3 mm and DD: 18 mm). The results of this test are also shown in Table 6.2 and are similar to all other results of the 18 mm pellets except one small difference; It is evident a small spike of gas production shown in Figure 6.10 at around the 80^{th} minute. The rapid increase of combustible gaseous species occurred due to the manual bed agitation. The lid at the top of the gasifier was opened and by using a metallic rod, the bed was agitated (or mixed) for exactly 1 minute. The opening of the lid can be observed in Figure 6.9 at around the same time that the temperature in TC2 drops rapidly. Immediately after the agitation, combustible gaseous products are produced. In order to test that the increase of gaseous species was due to the bed agitation and not due to the opening of the lid, the lid was reopened after about 20 minutes (around 100^{th} minute) but this time without agitating the bed. This time there was no syngas production and although it would require more testing in better controllable conditions it should be considered that the bed agitation would improve the gasification performance of the 18mm oilseed rape straw pellets. The method was not tested in other types of pellets thus it would be interesting to see if there would be an increase in the performance, of pellet types that already have shown high performance. Furthermore the method could be performed automatically with another type of grate. Rotating grates could be an alternative solution for improving the flexibility of the downdraft gasification unit, so that to allow extreme values of sizes. A rotating grate could also improve the gasification performance for another reason, which is the more efficient ash removal.

6.1.3 Relationship between downdraft gasification process and pellet quality

The first set of graphs in Figure 6.11 shows the relationship between the pellet density and the gasification quality parameters. In Figure 6.11a the relationship of pellet density and the higher heating value of the product gas is shown. It is clear that the pellets manufactured from the wet feed (14-17% moisture) have higher density, and the product gas heating value is lower. Between the pellets manufactured from feed with similar moisture content, the pellet density shows no relationship with the higher heating value. For example the first two points in the graph that represent the pellet types 1 and 2 (manufactured from dry feed) show no difference in the gas heating value indicating that at least within the range of 50 kg/m^3 difference the heating value does not change with a change of the pellet density. Figure 6.11b shows the relationship between pellet density and cold gas efficiency and similar as before, the wet feed manufactured pellets have higher density but the product gas has lower cold gas efficiency in comparison to the pellets that were manufactured using the dry feed. The figure 6.11c represents the relationship between the carbon conversion efficiency and the pellet density. The 18 mm pellets were added in this Figure despite the fact that there was no combustible gas that was formed but nevertheless the carbon was converted to CO_2. It is evident from this graph the slightly negative trend between the pellet density and the carbon conversion efficiency. The higher the pellet density the lower the conversion of the fuel carbon that takes place. This is due to the fact that the denser pellets are less porous and thus prevented the good interaction between the gasifying agents or the combustion products and the char.

Similar correlations can be observed in the following graphs. The correlation between the CO/CO_2 ratio and pellet density points out the lesser production of CO using denser pellets that were manufactured from the wet feed. Similar results are found in the correlation of pellet density with the mass conversion factor, the specific energy rate and the gasification rate. It is evident from this set of graphs that the wet feed resulted in an increased pellet density and their combination resulted in decreased gasification efficiency. The pellet pairs manufactured from the same feed (‘1,2’ and ‘3,4’), despite having slightly different pellet densities, have no difference large enough to justify a decreased performance. Pellets that were manufactured from a feed of similar moisture content, even if they have slightly different pellet density, are more likely to have similar gasification performance. However, pellets manufactured using feed with different moisture contents is more likely that their performance would be different and most probably their pellet densities would be different as well with the pellets manufactured from the wet feed will show higher densities and lower gasification performance.

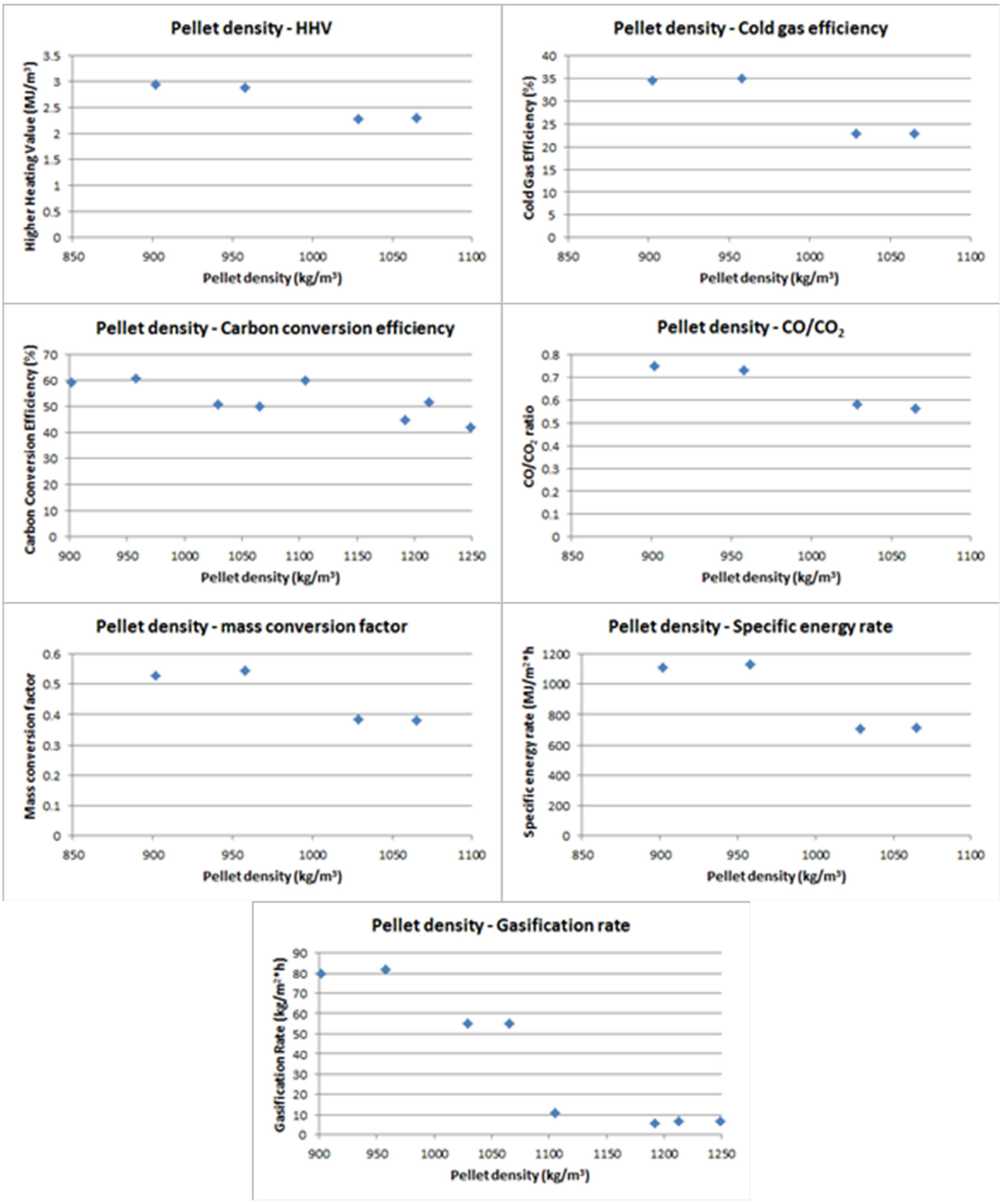

Figure 6.11: Relationship of the pellet density with the gasification quality parameters, a)Pellet density – HHV, b)Pellet density – Cold gas efficiency, c)Pellet density – Carbon conversion efficiency, d)Pellet density – CO/CO2, e)Pellet density – Mass conversion factor, f)Pellet density – specific energy rate, g) Pellet density – gasification rate

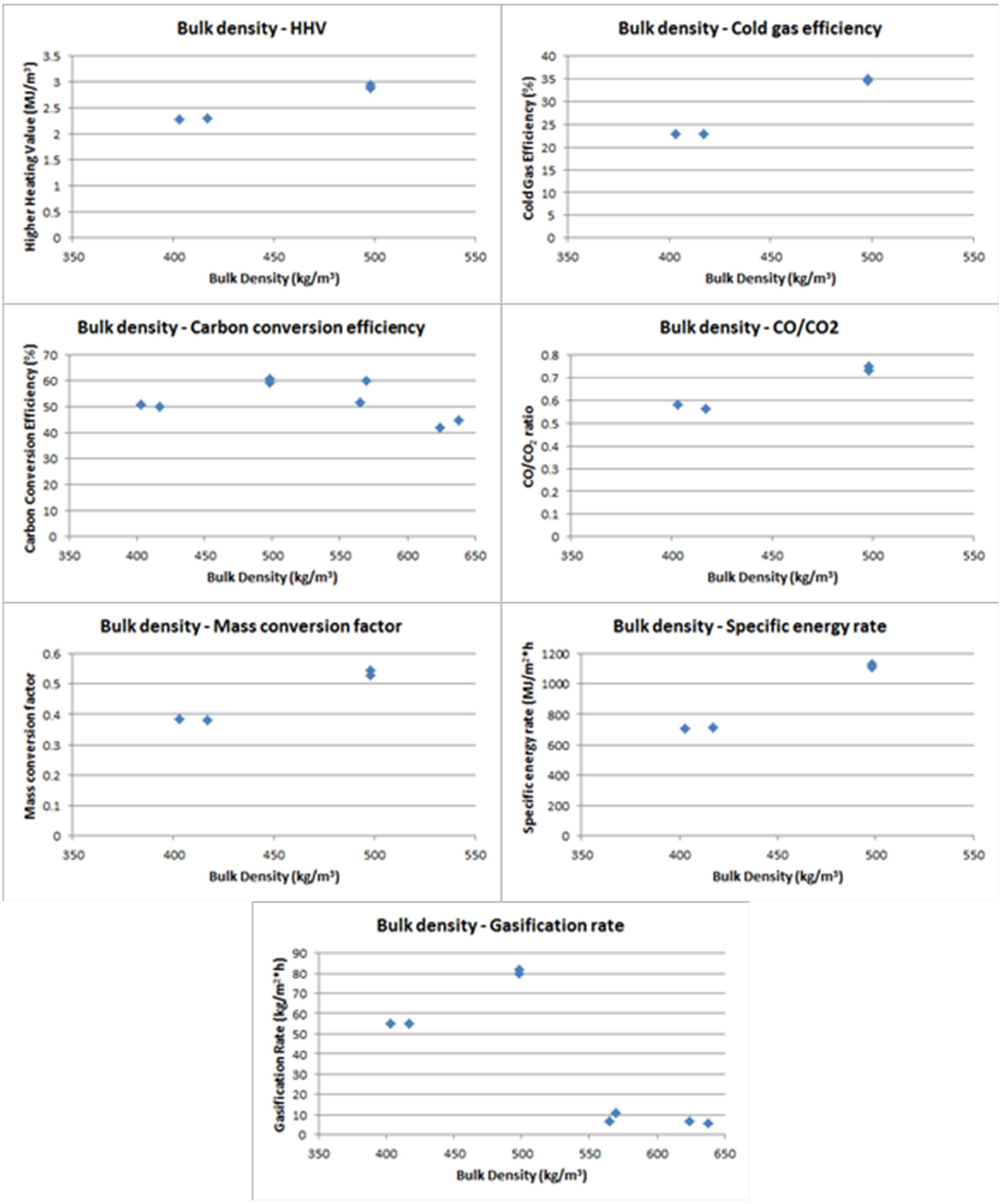

Figure 6.12: Relationship of the bulk density with the gasification quality parameters, a)Bulk density – HHV, b)Bulk density – Cold gas efficiency, c)Bulk density – Carbon conversion efficiency, d)Bulk density – CO/CO2, e)Bulk density – Mass conversion factor, f)Bulk density – specific energy rate, g)Bulk density – gasification rate

The graphs in Figure 6.12 show the relationship between the bulk density of the pellets and the gasification quality parameters. In Figure 6.12a the correlation between bulk density and the higher heating value of the gas is shown. The first two points represent the bulk density of the pellets manufactured from the wet feed, which is lower than the bulk density of the pellets that were manufactured from the dry feed. In general the increased bulk density is related with an increased HHV. Similar relations appear for the 5 mm pellets for all the other gasification quality characteristics. Concerning the carbon conversion efficiency the 5 mm pellets show similar relations, however the 18 mm pellets do not (Figure 6.12c). Similarly, the gasification rate is not clear as shown in Figure 6.12g for the 18 mm pellets. Pellets which are tolerable for the downdraft gasifier and manufactured using wet feed are more likely to have lesser bulk density and also decreased gasification performance. On the contrary, pellets manufactured from the dry feed, showed an increased bulk density which was also correlated with an increased gasification performance. Concerning only the 5 mm pellets, the bulk density of the pellets manufactured from similar feed (wet or dry) is too identical to identify any changes that might occur in the gasification performance using exactly the same pellets but different bulk densities.

The set of graphs provided in Figure 6.13 show the relationship of durability with the gasification quality parameters. In the Figure 6.13a we can observe the correlation between the durability and the gas higher heating value. Like the previous set of graphs, the relationships for the 5 mm pellets are generally positive. Figure 6.13a indicates that a higher durability may yield an increased HHV. The same is applied to the rest of the gasification quality parameters. Once more the relation is not clear in the case of 18 mm pellets concerning durability and carbon conversion efficiency and gasification rate. In general the pellets manufactured by using the wet feed exhibited lower durability and the lower durability is related with a decreased gasification performance.

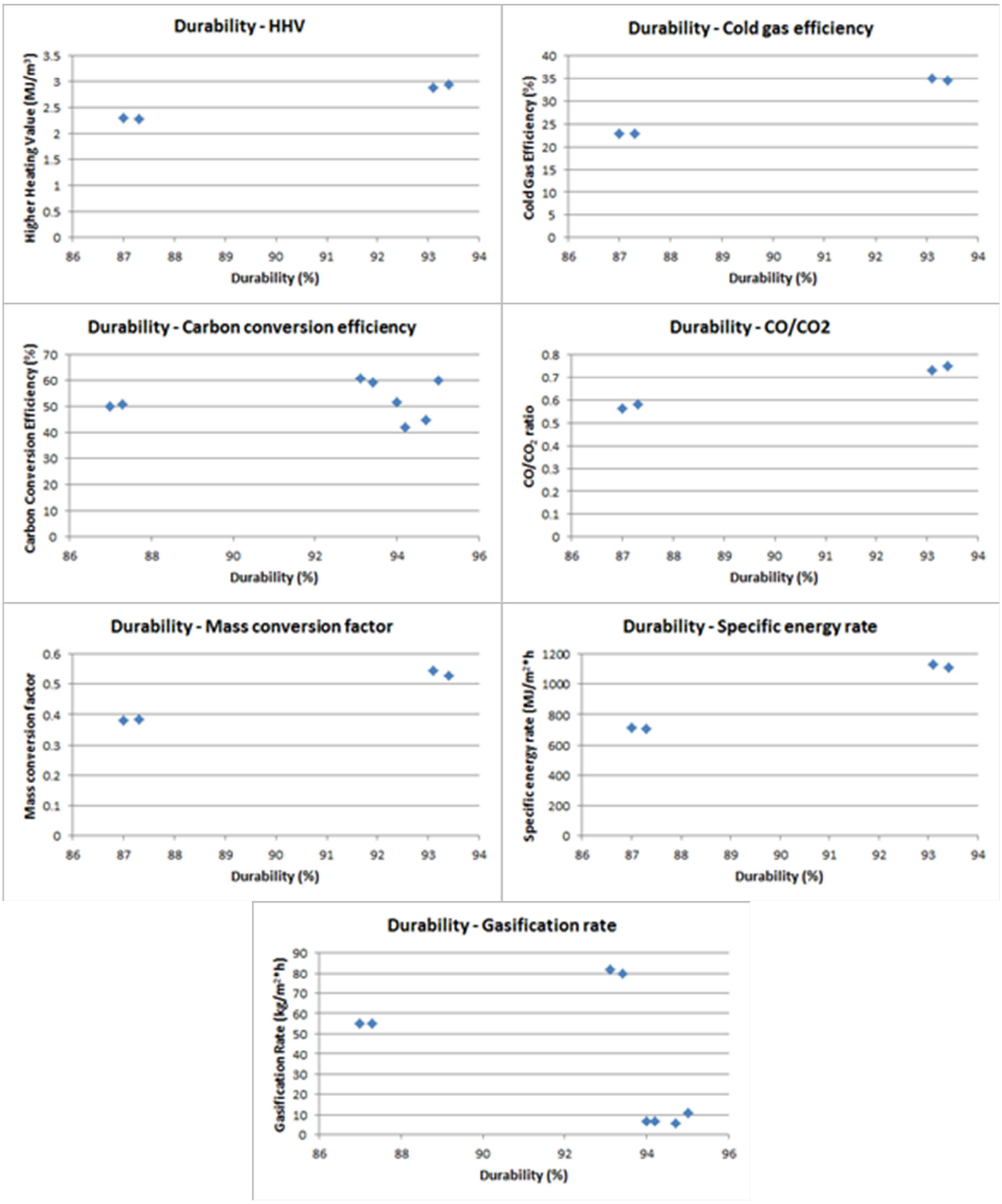

Figure 6.13: Relationship of the pellet durability with the gasification quality parameters, a)Durability – HHV, b)Durability – Cold gas efficiency, c)Durability – Carbon conversion efficiency, d)Durability – CO/CO2, e)Durability – Mass conversion factor, f)Durability – specific energy rate, g)Durability – gasification rate

6.1.4 Effect of pelleting parameters on the downdraft gasification process

This section discusses the effect of the pelleting parameters on the gasification quality parameters. The pelleting parameters are:

1. feedstock moisture content
2. feedstock particle size
3. die diameter

and the gasification quality parameters are:

1. higher heating value
2. cold gas efficiency
3. carbon conversion efficiency
4. CO/CO_2 ratio
5. mass conversion factor
6. specific energy rate
7. gasification rate

Graphs are presented in Figures 6.14-6.16 for all combinations except for the 18 mm which is only shown in the graphs concerning the carbon conversion efficiency and the gasification rate. The entire 18 mm range is represented only for the die diameter graphs, which it cannot be avoided because a comparison is made between the small and large pellets for downdraft gasification.

Figure 6.14 shows the effect of the feedstock moisture content (dry feed: 5-8%wt and wet feed: 14-17%wt) with the gasification quality parameters. The feedstock moisture content has an enormous effect on the quality of the pellets which in turn is reflected upon the quality of the gasification process. More specifically, the high feedstock moisture content is related with lower heating value and lower cold gas efficiency as it is shown in graphs 48a and 48b. The reason is that the pellets manufactured by the wet feed have also higher moisture content themselves, and also that the durability and bulk density of these pellets is lower. The decreased durability is an indicator of increased amount of fines which may hinder the passage of air through the grate. Furthermore, fines are more likely to be combusted rapidly and not form char which is essential for the production of gaseous species.

Similarly, the relation applies to the carbon conversion efficiency to both 5 mm and 18 mm pellets. The effect is also evident on the CO/CO_2 ratio indicating the low production of CO with increased moisture, and on the mass conversion factor indicating the overall decrease in the gasifier performance due to the dissipation of extra energy for the evaporation of the additional moisture. In turn the effect concerns also the specific energy and gasification rates by which the drop in both rates points out the general drop in performance with extreme high feedstock moisture.

A very dry feedstock requires more energy to be dealt with (dryers etc) but it will also provide a better gas in comparison to the very wet feed. The optimal solution would be a feedstock moisture of between 8-14%wt; within this moisture range, the benefits of both aspects are achieved in that the material is dry enough to be gasified, yet wet enough to be pelletised.

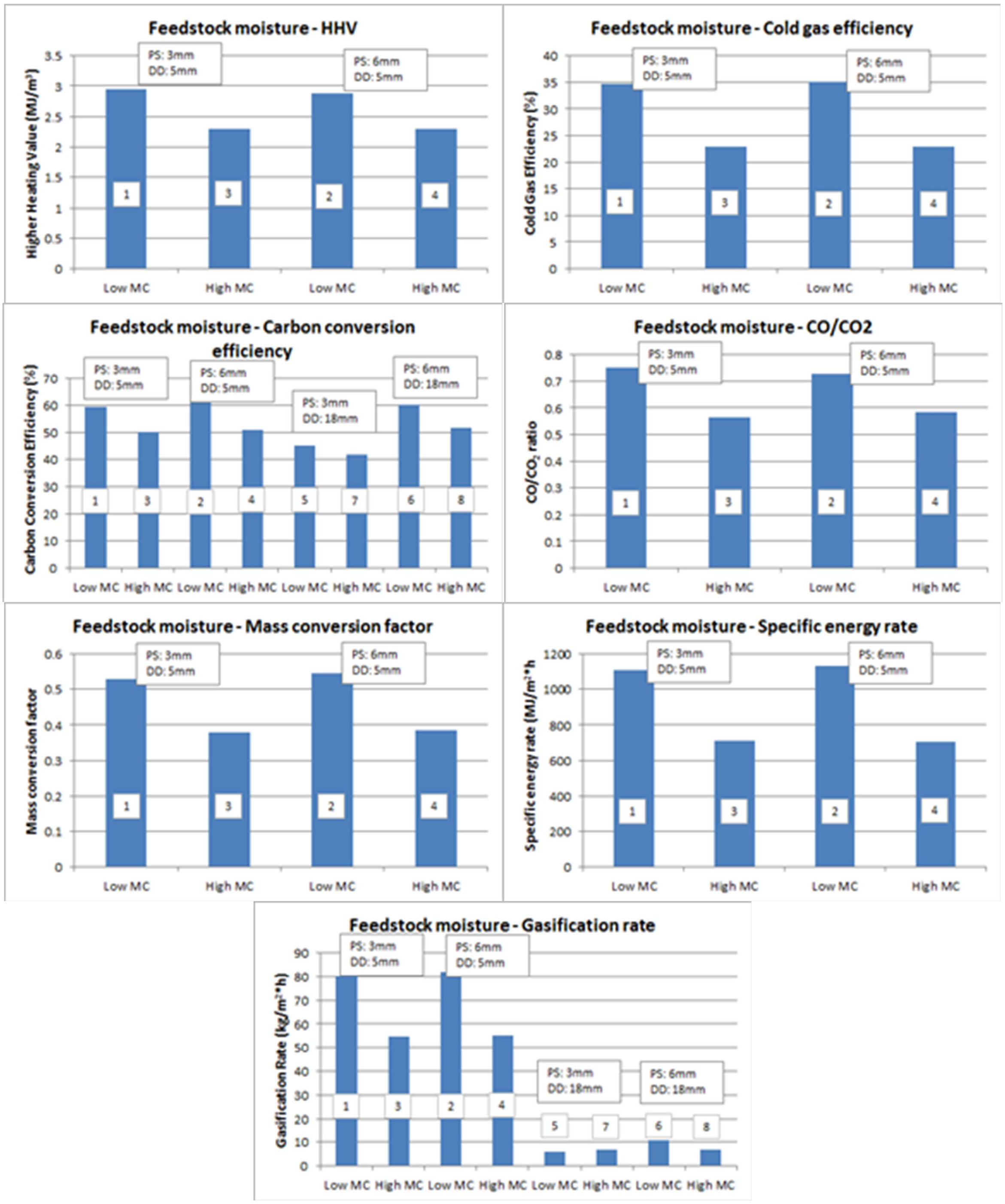

Figure 6.14: Effect of feedstock moisture content on the gasification quality parameters, a)Feedstock moisture – HHV, b)Feedstock moisture – Cold gas efficiency, c)Feedstock moisture – Carbon conversion efficiency, d)Feedstock moisture – CO/CO2, e)Feedstock moisture – Mass conversion factor, f)Feedstock moisture – specific energy rate, g)Feedstock moisture – gasification rate

Figure 6.15 shows the effect of feedstock particle size on the gasification quality parameters. All the results indicate that particle size have no influence in any gasification quality parameter with one exception. The carbon conversion efficiency in the case of the 18 mm pellets seems to increase with an increase of the particle size but it cannot be proven because the tests with the higher carbon conversion are also the tests with the higher equivalence ratio.

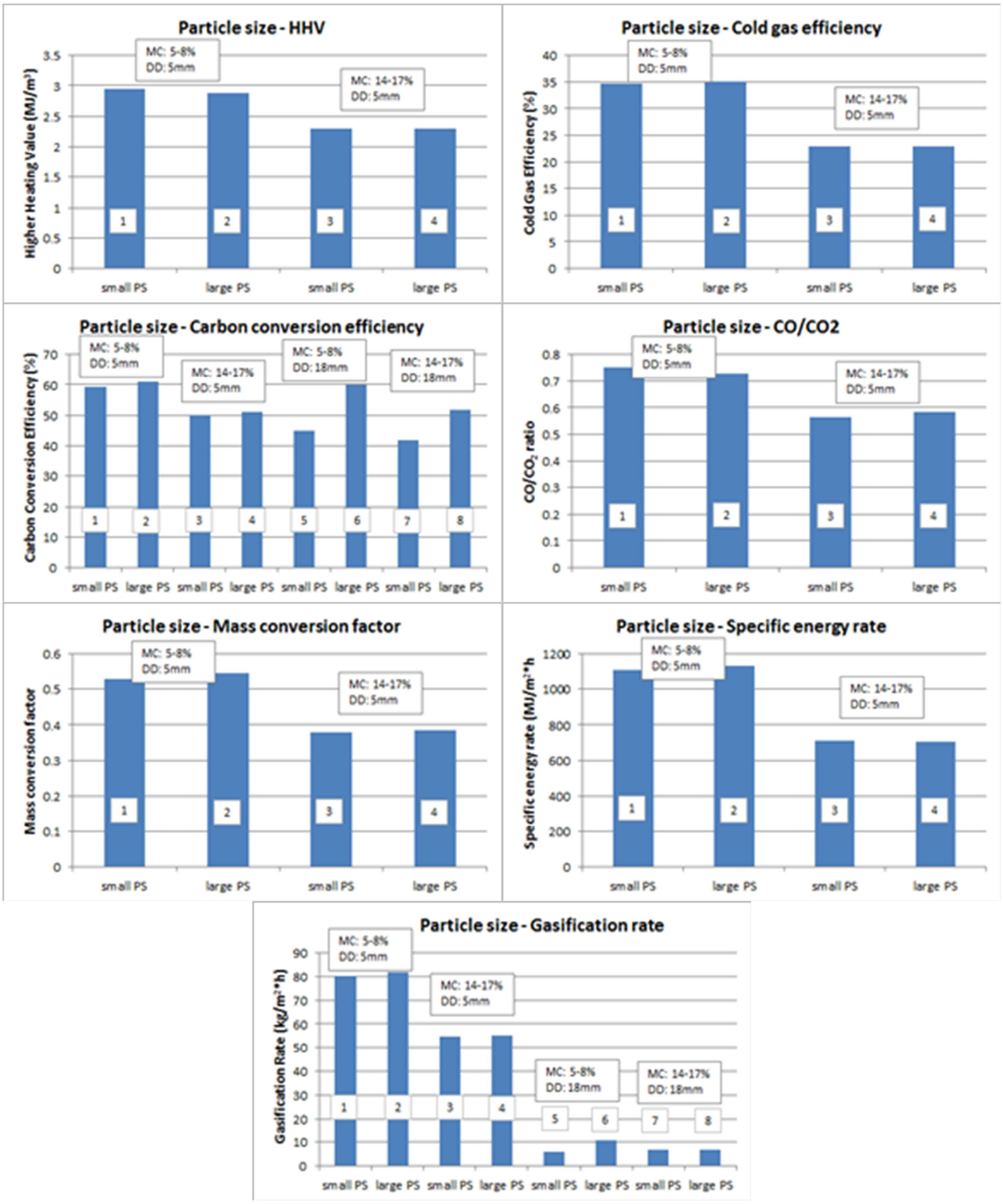

Figure 6.15: Effect of feedstock particle size on the gasification quality parameters, a)Particle size – HHV, b)Particle size – Cold gas efficiency, c)Particle size – Carbon conversion efficiency, d)Particle size – CO/CO2, e)Particle size – Mass conversion factor, f)Particle size – specific energy rate, g)Particle size – gasification rate

Figure 6.16 shows the effect of die diameter (5 mm and 18 mm nominal diameter) upon the downdraft gasification quality parameters. In the most of the cases the effect it is very clear in that the smaller pellets gasified whereas the large pellets did not. The main reason for this is the lack of tolerance of a downdraft gasification unit for fuels of large sizes. The reason for that will be better explained in the next section.

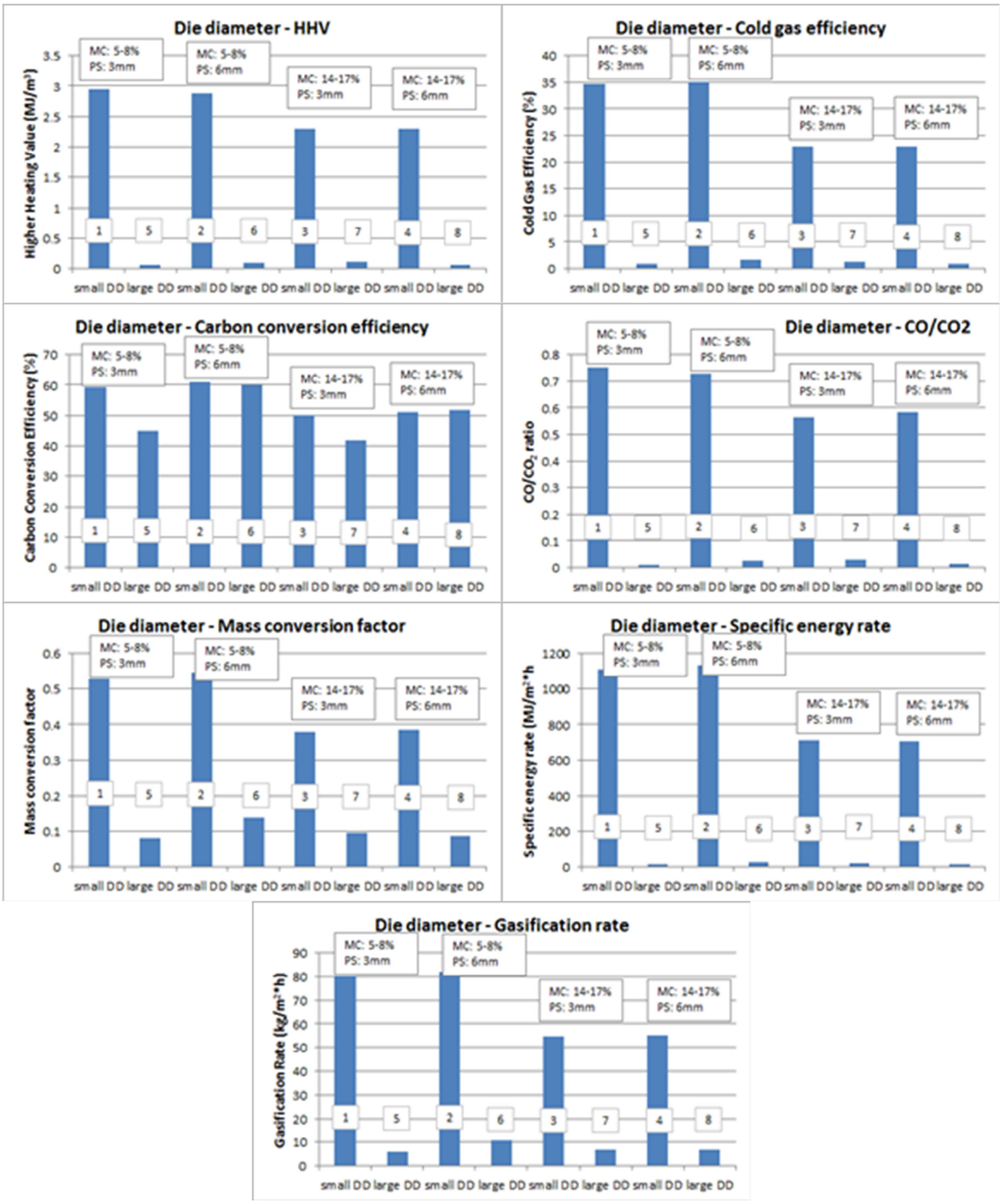

Figure 6.16: Effect of die diameter on the gasification quality parameters, a)Die diameter – HHV, b)Die diameter – Cold gas efficiency, c)Die diameter – Carbon conversion efficiency, d)Die diameter – CO/CO2, e)Die diameter – Mass conversion factor, f)Die diameter – specific energy rate, g)Die diameter – gasification rate

In Figure 6.16c, shows the effect of the die diameter on the carbon conversion efficiency where the carbon conversion for the pairs '2,6' and '4,8' are the same. This could be a coincidence due to the fact that the tests 6 and 8 were performed in high equivalence ratios. Furthermore, another interesting result is the evident effect of the moisture content. In every graph, the pellets manufactured using the wet feed showed lower response in comparison to the pellets manufactured using the dry feed.

6.1.5 Discussion

The initial effects upon the pellets were created by the pelleting manufacturing properties. The properties under investigation here are the feedstock moisture content, the feedstock particle size and the die diameter. These pelleting properties were related with the pellet quality in the previous sections and in turn were related with gasification performance.

One of the most important parameters of the pellet manufacturing process is the moisture content of the feedstock. In fact, the use of high moisture content feedstock formed pellets with a slightly higher pellet density, lower bulk density and lower durability. The two last properties are connected, due to the fact that a lower durability is the indicator of increased amount of fines and the bulk of fines have always smaller density than the bulk of pellets as we have already shown. Furthermore, the increased feedstock moisture content resulted in pellets with higher moisture content. Thus there are two different effects of feedstock moisture on the pellets. Firstly, the fact that the moisture content of the pellets themselves have increased with increased feedstock moisture content, and secondly the fact that the increased feedstock moisture content have changed the mechanical characteristics and the quality parameters of the pellets.

The literature provides extensive data and proof of what happens in the case of increased moisture content in a biomass fuel. The general notion in literature is an increase of H_2, CO_2 and CH_4 and the decrease of CO gas percentage with an increase of the moisture content and furthermore, the decrease of the gas heating value is reported [116, 117, 118]. In addition, lower conversion, pyrolysis and gasification rates are reported, that caused by the decrease of the temperature due to the increased moisture content and the heat loss due to the water evaporation [82, 119, 69].

Furthermore, it is reported that the increased moisture content it is also a cause for the decline of the cold gas efficiency and the conversion efficiency which is caused by the higher concentration of CO_2 and the lower of CO and also the incomplete water utilization [120].

The most of the cases mentioned, were observed in the experiments and analysis discussed in this chapter with one exception: the increased amount of H_2 and CH_4. In fact, in the case of the wet pellets, the percentage of H_2 and CH_4 was lower or at most equal to the one of the dry pellets. This could be due to the fact that the pellet moisture isn't as significantly different as to justify such large effects on the percentage of gaseous species. Thus, it can be said that the effects caused by the feedstock moisture content upon the physical characteristics of the pellets, in this case were greater than the actual moisture content of the pellets, which regardless did also play a considerable role.

The increased feedstock moisture had a positive effect upon the pellet density, and a negative effect upon the bulk density and the durability of the pellets, especially the in 5 mm pellets. At the same time the feedstock particle size did not have any considerable effect upon the three pellet quality parameters while the die diameter had a positive effect in all of them. Although some clear correlations were made between the parameters in the previous chapters, one of the important outcomes of this chapter was the complete failure of gasifing the large OSRS pellets in a downdraft gasifier. An explanation of this effect will follow along with an explanation of the rest of the phenomena that were observed previously.

Gasification is an extremely complex conversion process involving homogenous and heterogeneous, exothermic and endothermic reactions. In gasification, chemical reaction and transport phenomena play a role in the overall conversion. At low temperatures the rate determining factor is the chemical reaction, but in high temperatures the pore-diffusion is the controlling step [121]. The process of gasification generally occurs only in a thin zone on the particle surface while the internal pore structure of the particle remains essentially intact. The increase of temperature in high values and the extended time of exposure can cause thermal annealing (structural re-ordering of the amorphous biomass) resulting in a decrease of the concentration of active sites [122]. Thermal annealing was observed in the gasification of the large 18 mm pellets. Typically in low heating rates, the particle porosity allows the volatile release with no major deformations of the char matrix. On the other hand, in high heating rates the char and cell structure may melt after the devolatilization and plastic deformations are likely to occur [123]. This is one possible reason of the low quality of gasification of the 18 mm pellets and the large agglomerates that were formed in the bed (Figure 6.17). In this case, volatiles were combusted, rapidly increasing the local bed temperature; Due to the limited amount of available active sites and lower reaction rates because of their higher pellet density, the endothermic gasification reactions did not occur. The decreased effect of pore diffusion could also explain the decrease of the gasification efficiency with all the pellets that had higher pellet density.

Figure 6.17: Agglomerates and residues in downdraft gasification of OSRS pellets of: a)type 2, b)type 8, c) type 7 (scale: 15 cm ruler)

The heat transfer by radiation is the main cause for the initiation of the pyrolysis of biomass. The incandescent particles heat up the gas-air mixtures and the mixed gases combust producing more energy. This energy is emitted back to the solid particles through heat transfer by radiation and at that point the temperature of the solid biomass increases. It is also at this point that char oxidation reactions takes place. This cycle is also used to dry and pyrolise the fresh biomass that enters the reactor [124]. It is clear here that since the active sites of the 18 mm pellets are in limited numbers, the char oxidation after the volatile combustion becomes the dominant conversion method of the large pellets since the oxidation reactions are by far more rapid than the reduction reactions. In addition the channelling formed because of the melting of biomass cells due to the high temperatures could also explain the behaviour of the large pellets. The syngas production is affected by the bed's available reactive area which is a function of the degree of channeling in the bed [125]. The conversion of the large pellets was unsuccessful because there were no reduction reactions taking place.

There could be other reasons for the failure of the 18 mm pellets to be gasified. In general the individual pellets in the bed have larger space between them in the 18 mm pellet's case than in the 5 mm pellet's case. The porosity of the char bed is the dominant factor of pressure drop [126] and in our case since the gasification unit works by sucking air (inducing negative pressure) and not blowing air could have just passed at high velocities without any difficulty, which could be one more reason for the quickest reactions (oxidation reactions) to occur. The bulk bed porosity can be seen in the Table 6.3.

Table 6.3: Bed porosity of the OSRS, Miscanthus and DDGS pellets

Pellet type	**Bed porosity (%)**
5mm OSRS	31.25 ±6.8
18mm OSRS	37.2 ±4
E-on Miscanthus	19.9
DDGS	30.1

One study suggests that pellets with different sizes have different gasification rates but no different pyrolysis rates; the larger the pellet is, the slower the gasification would be [78]. Furthermore the smaller the particle diameter (no less than 0.5 cm) leads to an improved conversion efficiency due to the fewer diffusional limitations [82]. On the contrary, a different study suggested that the particle size has an effect upon the pyrolysis time; the larger the size is, the longest the pyrolysis time would be at similar temperatures [69]. A different study suggests that the heating rate in pyrolysis phase is a function of the particle size. In large particle sizes the heating conditions are different on the surface than the internal part of the particle. Thus, the reactivity decreases for char that was produced from thick or densified particles [73]. In addition, pellets with higher density resulted in a higher char yield [78].

It is generally assumed that an increase in the biomass size promotes the internal heat transfer resistance, results in greater temperature gradients in the biomass particle and lower temperatures in the internal than in the external of the particle. Thus it is typical that the small particle sizes lead to higher gas yield and carbon conversion efficiency. However, there are other cases where there is no clear indication of this effect and also cases that the changes in particle porosity result in a decline of the reactivity with a decreasing particle size [127]. Furthermore the same study suggested that while at the same gasification temperature, the smaller the particle size is, the weaker the influence of residence time is, and that a reduced period of time required for completion of gasification. The reason for the latter could be the increased heat transfer characteristics of the bed which in turn is a result of the increased thermal conductivity of the particles resulting basically in a higher speed of reaction [127].

The general results of the study showed that residence time was more important than the particle size and at higher temperatures decreased the effect of particle size. The effect of particle size (0.15-3 cm) on the gas yield and the carbon conversion efficiency was not significant [127]. Thus it is important to point out the different opinions in the literature about the effect of size on char gasification [128]. This could be due to the differences in the catalytic effect of the different ashes among the biomass fuels.

The char yield from large pellets is higher than the char yield from small pellets. Possible explanations could be the increased heat transfer resistance, the decomposition of the outer layer of the large pellets and the collapse of the pores that leads to prevention of mass transport due to the possible longer residence times and high temperature flames. Another explanation could be the melting of the ash within the pellets especially in the large pellets due to the fact that they were exposed in high temperatures for a longer period of time in comparison with the small pellets [129].

Concerning the char gasification thermodynamics it is shown in the literature that the amount of carbon that reacts with the pyrolysis products is limited by the heat content of the pyrolysis products. Thus the Boudouard reaction is generally incomplete in downdraft gasifiers (possibly 1-5% char remains) due to the endothermic nature of the gasification reactions. There are also mechanical reasons for the incomplete char gasification in the downdraft gasifiers. In fact, when char reacts with the combustion products these reactions occur mainly at the inner surfaces of the biomass. Under these conditions the thinner parts of the structure will be dissipated first leaving the cell wall vertices as fine dust. The fine dust is then entrained with the gas flow [130]. However, Standish *et al* reports a decrease in size of charcoal particles (10-30 mm) with conversion and also reported the stability of density at constant levels until 75% conversion which ones more it could mean that the gasification process takes place on the outer shell of the charcoal particles [128].

In general, the consumption rate is inversely proportional to the biomass size due to the increased reaction area in smaller particle sizes [124]. But usually it is not as simple for coals. It was found for coals that the bituminous coal that has a larger surface area than the anthracite has a smaller measured reactivity. This means that the magnitude of the surface area is not the dominant factor for the reactivity and the gasification in general but rather the quality of the surface and the accessibility of this surface. So there is a difference between the total surface area and the active surface area. A positive correlation was found between the active surface area and reactivity [121]. The reactivity of coals drops with the particle size as mentioned in the study [121]. The active and available carbon sites are a factor with higher weight in the gasification in comparison to the total surface area of the char which have no relevance to the reactivity [131]. Furthermore, in the case of the most of the coals, the reactivity decreases with an increasing conversion. But for the most of the biomass the reactivity increases with increasing conversion [132] which it could be possible due to the catalytic behaviour of the ash.

Concerning the durability, the pellets with lower durability (more fragile) could create a char dust layer above the grate and that could lead to a rapid increase of pressure drop and the prevention of the gases to pass through [129] leading to a decreasing gasification efficiency. The low durability pellets formed fines which also reacted in a different manner in comparison with the pellets. For fine particles Mani *et al,* showed a decline of reactivity as particle size increases. The authors attributed this, to the larger surface area of the fine (smaller) particles; also implying that pore diffusion is limiting the reaction rate in any particle size except the fine particles [133]. In addition, for particle sizes below 1 mm, the pyrolysis process is controlled by the primary pyrolysis reactions but for particles greater than 1 mm, is controlled primary and secondary and also the heat transfer. As the particle size and the pyrolysis temperature increases the impact of the secondary reactions and the impact of heat transfer increases [134]. Thus, the fine particles formed from pellets with low durability appear to cause certain phenomena. On one hand, they rapidly convert with no diffusion limitations, thus having different reaction rates than the pellets, and on the other, they quickly form a layer of ash and inert char that could hinder the passage of the gases through the grate. Furthermore, only the primary pyrolysis reactions are responsible for the conversion of fine particle which it could lead to the increased amount of tar production. This could be one of the reasons for the lower gasification efficiency from pellet with lower durability.

In summary, the main phenomena that were observed during the downdraft gasification of the OSRS pellets were the feedstock moisture content and the die diameter while the feedstock particle size have no effect upon the gasification process. The increase of feedstock moisture increases the pellet density which may lead to lower reactivity of the biomass, as well as increasing the moisture of the pellet themselves leading to further reduction of conversion.

Pellet durability has also an impact for the reasons mentioned in the previous paragraph. The size of the pellets played a great role in the downdraft gasification process. The 18 mm pellets could not be gasified due to numerous reasons, such as the melt of the outer layers, the agglomeration, the channelling, the increased temperature gradients, the bed porosity, the higher densities and the decreased amount of active carbon sites.

6.2 Spouted fluidised bed gasification of oilseed rape straw pellets

This section discusses the performance of the oilseed rape straw pellets in the spouted fluidised bed gasification unit. In the following subsections, the gasification performance of the 5 mm, in the first section, and the 18 mm, in second section, OSRS pellets will be shown. In the subsections that follow, the spouted fluidised bed gasification process is correlated with the pellet quality and in the next subsection with the pelleting parameters. Lastly, the results are discussed in the last subsection.

6.2.1 Gasification of the 5 mm OSRS pellets

The results of the gasification of the 5 mm OSRS pellets are presented in Table 6.4 in the ER range of 0.16-0.25. Results from Table 6.4, were taken for comparisons later on (in the graphs). Bold letters are used to denote the No. of the test that was used for this purpose.

The data in Table 6.4 were slightly different. The CO percentage lay within the range of 4.4-8.6% while the CO_2 percentage is steadily retained in high levels. H_2 reaches the 5% production, with values as low as 1.1% while CH_4 lay within the range of 0.9-3.1%. Consequently, the heating value of the gas reaching 3 MJ/m^3 with values as low as 1 MJ/m^3. The cold gas efficiency reaches as high as 21.5% with the lowest value of 7.2%. On the other hand, the range of carbon conversion efficiency reached values only as high as 42% with the lowest values close to 29%. The main reason for this is the low amount of air feed input in which low amounts of fuel were converted (mostly in CO_2). Nevertheless, the values of Table 6.4 were chosen to be compared with the table values of the next section due to the similar ER range. Further data for spout bed gasification of 5 mm pellets are in Appendix B.

Table 6.4: Performance of the 5 mm oilseed rape straw pellets in a spouted fluidised bed gasifier within the ER range: 0.16-0.25

		OSRS pellet type						
		1	**2**	2	**3**	3	**4**	4
Biomass feed (kg/h)		6(1)	6(1)	7(2)	7(2)	6(1)	9.5(3)	9.5(3)
Air feed (l/min)		125(4)	125(4)	125(4)	125(4)	125(4)	175(5)	125(4)
Equivalence ratio		0.23	0.23	0.2	0.21	0.25	0.22	0.16
Average gas composition	CO	8.43	8.06	9.4	6.9	4.4	6.95	8.6
	CO_2	18.5	17.6	19	17.7	16.9	17.4	18.6
	H_2	4.2	3.8	5	2.52	1.1	2.63	4.8
	CH_4	2.46	2.4	3.1	1.73	0.9	1.87	2.5
	N_2	66.41	68.14	63.5	71.15	76.7	71.15	65.5
Gas yield ($m^3/kg_{biomass}$)		1.5	1.46	1.34	1.2	1.3	1.23	0.96
HHV (MJ/m^3)		2.6	2.47	3	1.88	1.06	1.96	2.7
Cold gas efficiency (%)		20.2	18.9	21.5	11.7	7.2	12.5	13.3
Carbon conversion efficiency (%)		42	39.1	40.5	31.7	29	32.6	28.7
CO/CO_2 ratio		0.455	0.458	0.49	0.39	0.26	0.399	0.46
Mass conversion factor		0.4	0.34	0.42	0.238	0.152	0.24	0.26
Specific energy rate (MJ/m^2*h)		1295	1209	1614	879	460	1280	1367
Gasification rate (kg/m^2*h)		120	102	146	84	46	115	126

(1)Error (SD): ±0.375kg
(2)Error (SD): ±0.37kg
(3)Error (SD): ±0.376kg
(4)Error: <5%, ±6.25 l/min
(5)Error: <5%, ±8.75 l/min

Temperature profiles and gas compositions are presented in the Figures 6.18-6.21. Efforts were made to keep the temperature below 800-850^{o}C due to the reason that bed was de-fluidizing every time the temperature was exceeding this value. The temperature was controlled by injection of appropriate quantities of nitrogen.

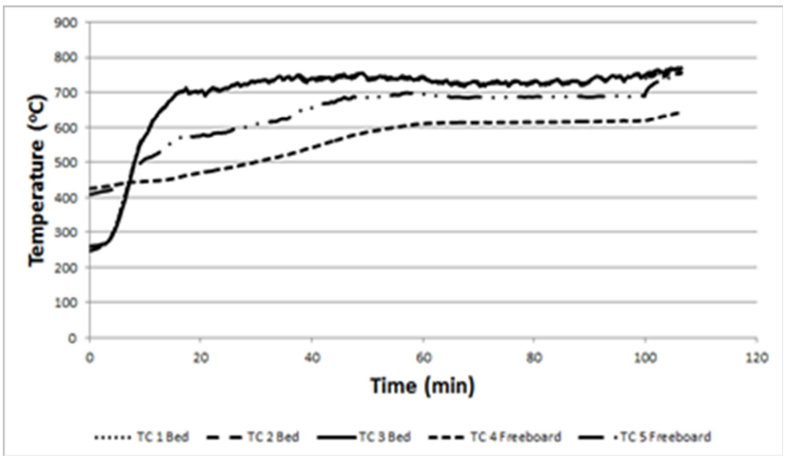

Figure 6.18: OSRS pellets type 1 temperature profile in a spouted fluidised bed gasifier

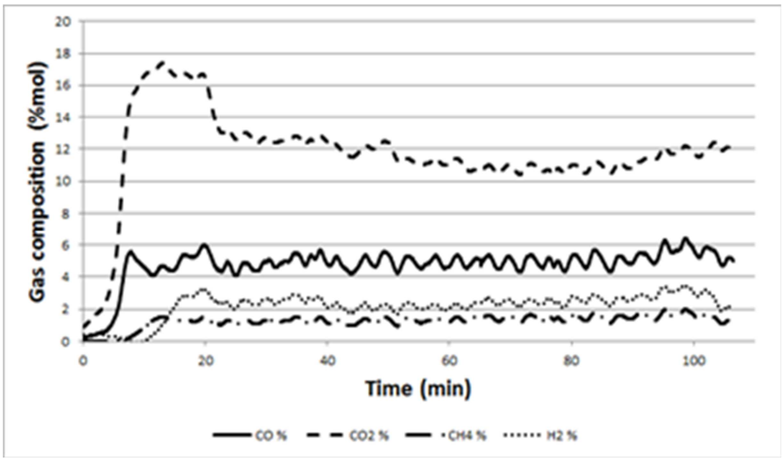

Figure 6.19: OSRS pellets type 1 gas composition in a spouted fluidised bed gasifier

Figures 6.18 and 6.19 present the graphs for temperature profile and gas composition respectively for the spout bed gasification of OSRS pellets type 1. As it can be seen the temperature was kept below the 800-850^{o}C to avoid de-fluidization. The first three thermocouples (TC1-3) in Figure 6.18 represent the temperature in three different sections of the bed, and as it can be observed, they overlap each other which mean that the bed sand is circulated and mixes well without any de-fluidization observed. The two next thermocouples (TC4 and 5) represent the temperature just above the bed and into the freeboard and it is clear that the temperatures here are lower than that of the bed. Figure 6.19 shows the online measurement of gas composition. The composition of the gaseous species remained constant throughout the whole test although minor changes in the input biomass and air feed was always tried to understand the process better and achieve better results.

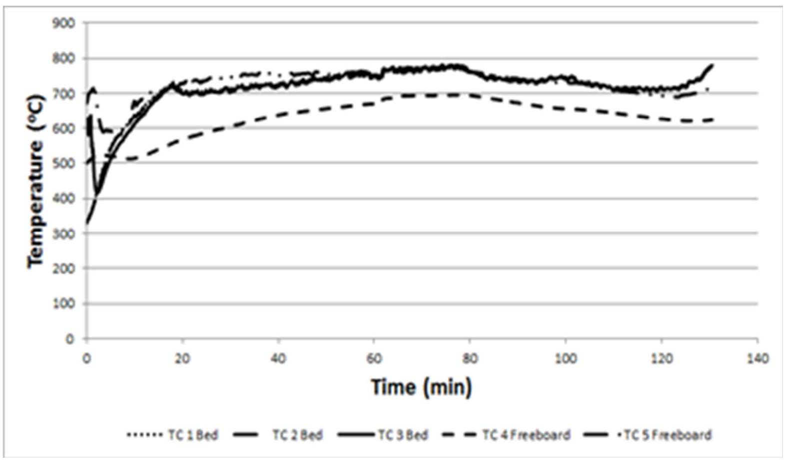

Figure 6.20: OSRS pellets type 4 temperature profile in a spouted fluidised bed gasifier

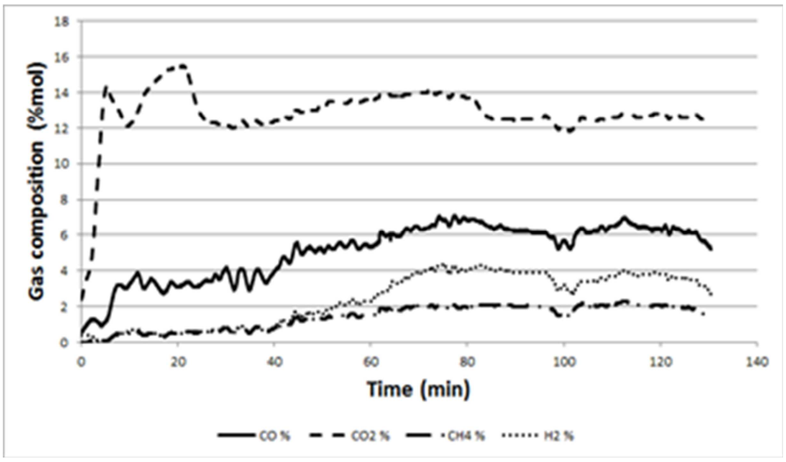

Figure 6.21: OSRS pellets type 4 gas composition in a spouted fluidised bed gasifier

Efforts were made to improve the gasification efficiency of the OSRS pellets in various ways because the efficiency was not as high as other tests presented in the literature. An example of these efforts is shown in Figure 6.21 in which the output gas concentration is shown after the alteration of the input biomass and air feed conditions. The first half part (0-70 minute) shows an upward trend in syngas and represents ER values in the range between 0.3 decreasing to 0.22. The second half (70-140 minute) represents ER values from 0.22 to 0.11. The big advantage of the spouted fluidised bed rig is that any minor alterations made in the input conditions, the output signal was immediately responding and quickly reaching the new steady state condition (between 5 and 10 minutes). Any major changes of the input conditions could reach the steady state within 20 minutes. This fact helped whenever different combinations of input conditions were implemented.

6.2.2 Gasification of the 18 mm OSRS pellets

In this subsection the gasification performance of the 18 mm OSRS pellets in a spout bed gasifier will be presented. An important remark in this section is that, after the exhaustion of all possible combinations in order to increase the gasification efficiency of the OSRS pellets, it was found to be prudent to mix the OSRS pellets with Miscanthus pellets and investigate the outcome. The type 8 of OSRS pellets were fed into the gasifier, mixed with E-On Miscanthus pellets at a percentage of 50-50%. For this reason, the type 8 OSRS pellets will be treated as a co-gasification test at 1:1 ratio by weight. Furthermore, once again, the bold numbering represents the tests that were chosen for the comparison of the parameters later on.

In Table 6.5 the results within the ER range 0.21-0.25 are shown. CO varies from 6.1 to 12.1% and the CO_2 is high in the most of the cases. The percentages of H_2 and CH_4 are within the ranges of 3-8.4% and 1.5-3.6% respectively. The gas yield reaching the 1.51 m^3/kg, with a minimum of 1.265 m^3/kg, while the gas heating value reaches the value of 4 MJ/m^3, with a minimum value of 1.78 MJ/m^3. The cold gas efficiency lay in the range of 11.7-31.9% while the carbon conversion efficiency lay in the range of 29.8-54.6%. Further data for the spouted fluidised bed gasification of 18 mm pellets are in Appendix B.

Table 6.5: Performance of the 18 mm oilseed rape straw pellets in a spouted fluidised bed gasifier within the ER range: 0.21-0.25

		OSRS pellet type				
		5	**6**	**7**	**8**	8
Biomass feed (kg/h)		8.5$^{(1)}$	6.5$^{(2)}$	6.5$^{(2)}$	7.05$^{(3)}$	8.05$^{(4)}$
Air feed (l/min)		175$^{(5)}$	125$^{(6)}$	125$^{(6)}$	125$^{(6)}$	150$^{(7)}$
Equivalence ratio		0.227	0.21	0.23	0.23	0.245
Average gas composition	CO	6.9	6.8	6.1	9.75	12.1
	CO_2	18.7	15.7	16.8	16.9	17.1
	H_2	3.7	3	3.13	8.2	8.4
	CH_4	1.72	2.05	1.54	2.73	3.6
	N_2	68.98	72.45	72.43	62.42	58.8
Gas yield ($m^3/kg_{biomass}$)		1.42	1.265	1.27	1.35	1.51
HHV (MJ/m^3)		2.03	2.05	1.78	3.36	4
Cold gas efficiency (%)		15	13.6	11.7	23.7	31.9
Carbon conversion efficiency (%)		37.2	29.8	31.3	43.7	54.6
CO/CO_2 ratio		0.369	0.436	0.363	0.58	0.7
Mass conversion factor		0.33	0.194	0.21	0.355	0.485
Specific energy rate (MJ/m^2*h)		1372	942	822	1797	2755
Gasification rate (kg/m^2*h)		141	64	68	131	204

(1)Error (SD): ±0.336kg
(2)Error (SD): ±0.34kg
(3)Error (SD): ±0.374kg
(4)Error (SD): ±0.318kg
(5)Error: <5%, ±8.75 l/min
(6)Error: <5%, ±6.25 l/min
(7)Error: <5%, ±7.5 l/min

Figures 6.22 and 6.23 represent an example of the gasification performance of the 18 mm pellets. Once again, an effort was made to keep the temperature below 800-850^oC to avoid de-fluidization of the bed. An important remark in this example that applies to all the 18 mm pellets gasification is the rapid and enhanced fluctuations of the gas composition possibly due to the large size of the pellets. Despite the fact that the velocity of the screw feeder was in similar levels as in the gasification of the 5 mm pellets, the pellets fed in a different manner somehow more random, thus the formation of fluctuations seen in Figure 6.23.

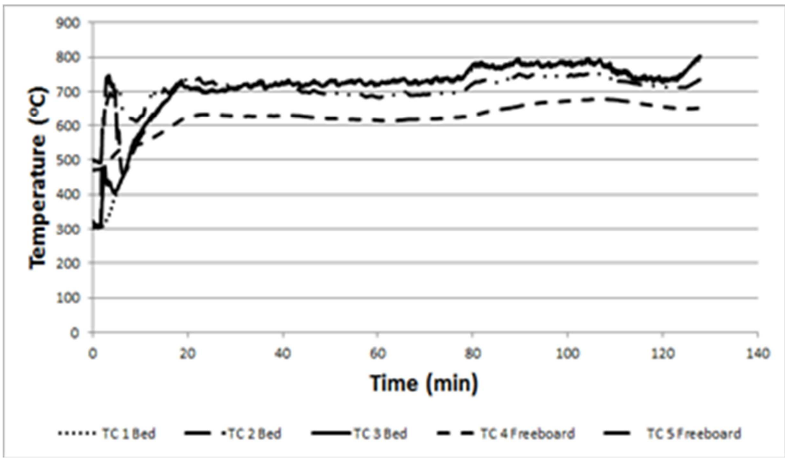

Figure 6.22: OSRS pellets type 6 temperature profile in a spouted fluidised bed gasifier

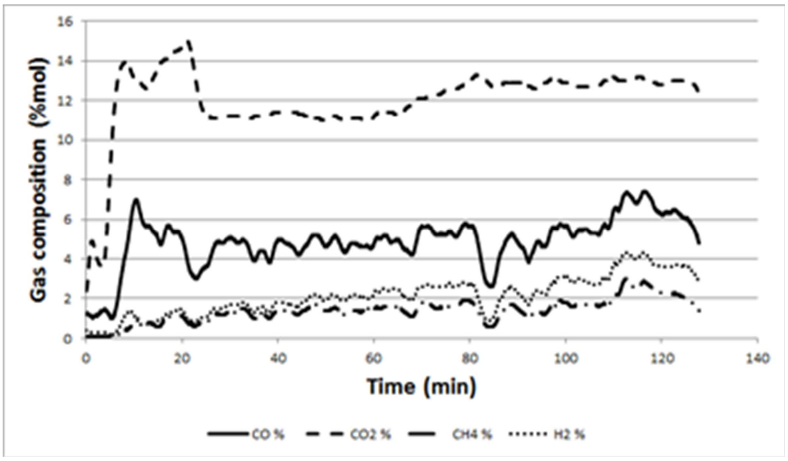

Figure 6.23: OSRS pellets type 6 gas composition in a spouted fluidised bed gasifier

6.2.3 The relationship of spouted fluidised bed gasification process with pellet quality

In Figure 6.24 the relationship between the pellet density and the gasification process are presented. Except in the case of specific energy rate and the gasification rate, it is seems that the pellet density is related in a negative manner with gasification parameters. An important exception it can be observed in the co-gasification test which always seems to be either the highest or among the highest values in each specific case. Thus, it is not only the pellet density that plays a role in the gasification process, but instead is the quality of the surface reactions as it was shown in the previous chapter (see section 6.1.5).

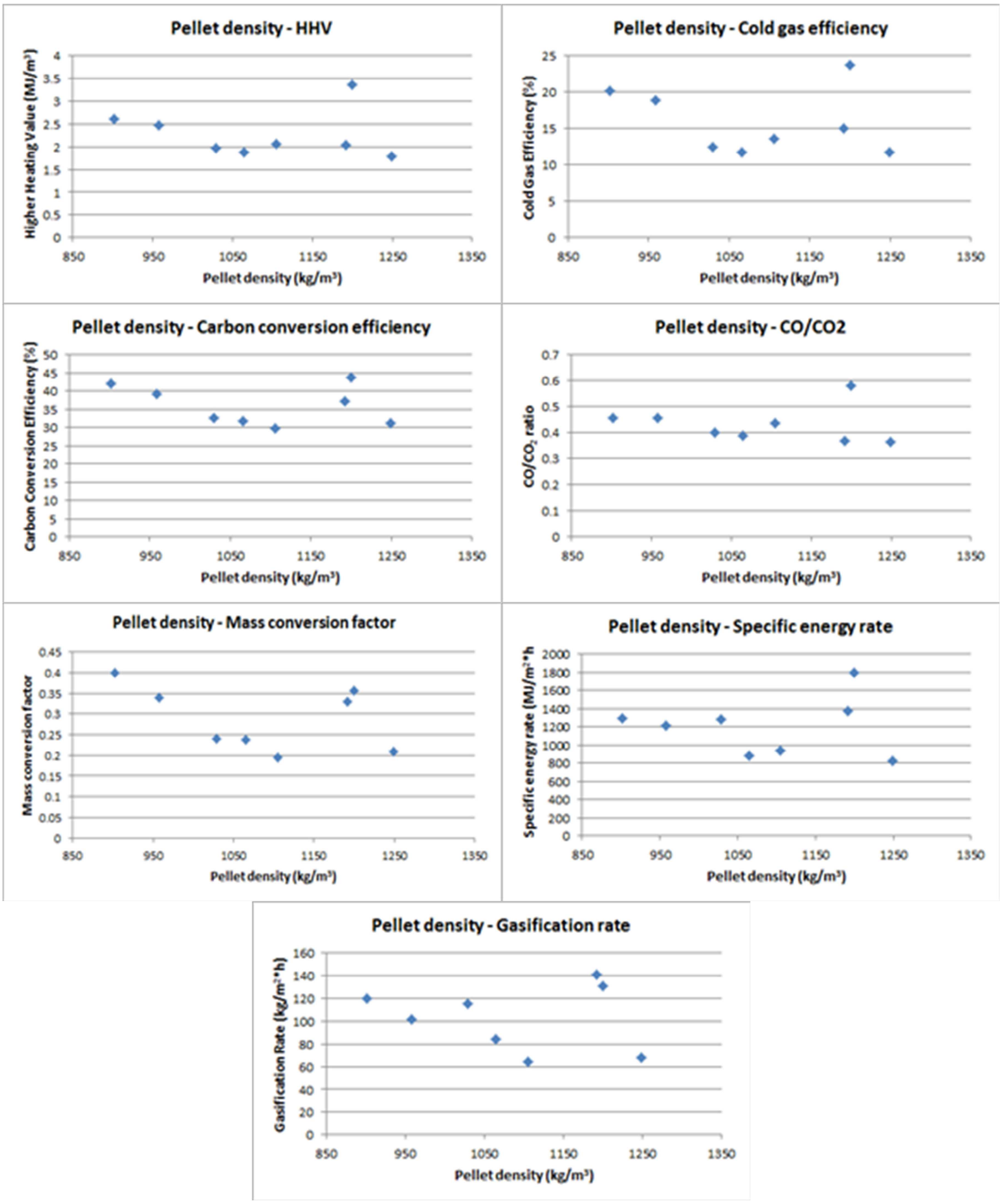

Figure 6.24: Relationship of the pellet density with the gasification quality parameters, a)Pellet density – HHV, b)Pellet density – Cold gas efficiency, c)Pellet density – Carbon conversion efficiency, d)Pellet density – CO/CO2, e)Pellet density – Mass conversion factor, f)Pellet density – specific energy rate, g) Pellet density – gasification rate

The correlation of bulk density and the parameters of the gasification process are shown in Figure 6.25. Similar trend it can be observed for all the graphs again with the exception of specific energy rate and gasification rate. It seems that the trend for the 5 mm pellets is positive but somehow is not clear for the 18 mm pellets. Furthermore, the trend of the 5 mm pellets is similar to one in the case of downdraft gasification. In overall terms though, the bulk density shows a relationship in the case of the 5 mm pellets but it does not in the case of the 18 mm pellets. Furthermore, the case of the co-gasification, shows that in nearly all the graphs has the highest value.

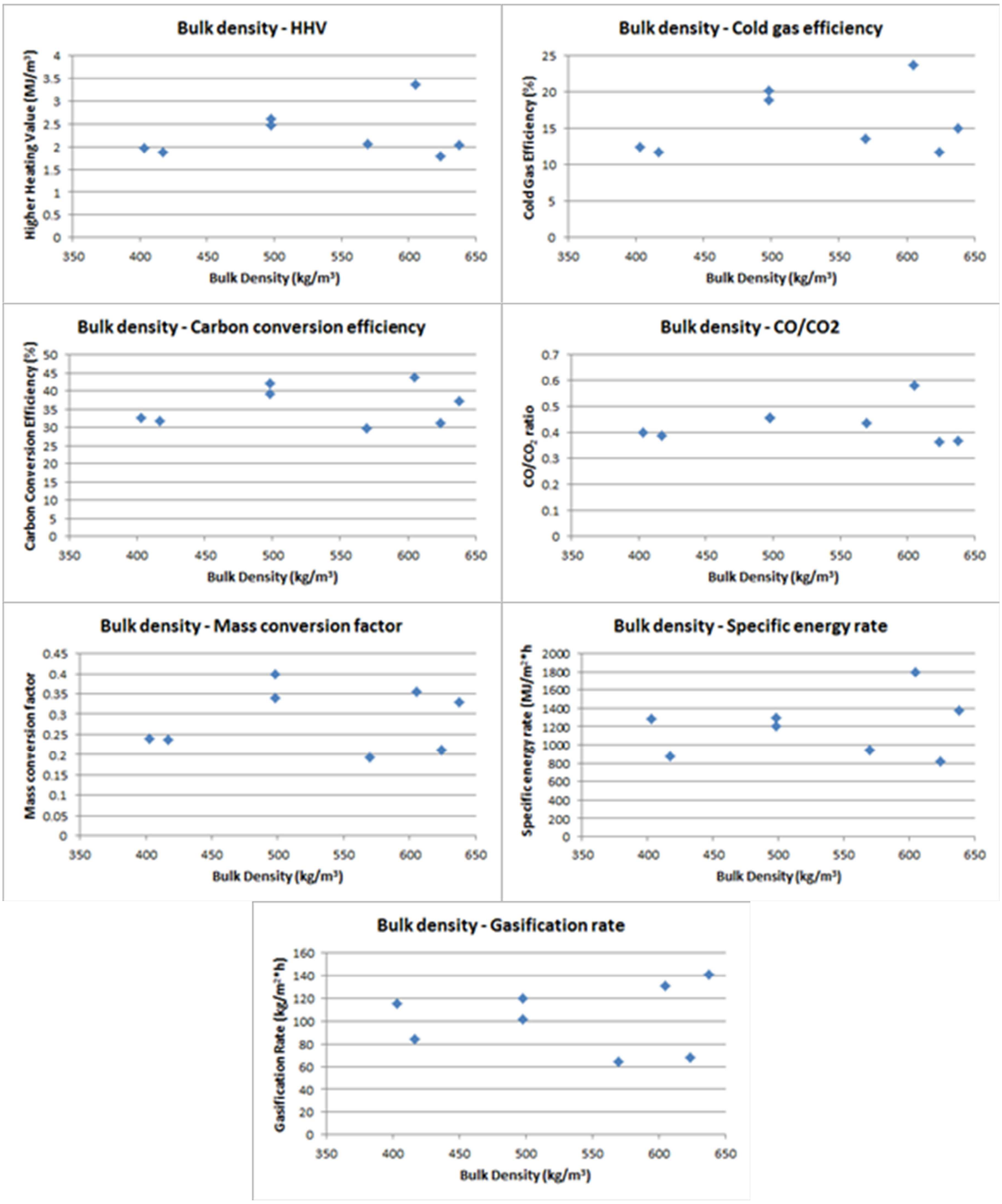

Figure 6.25: Relationship of the bulk density with the gasification quality parameters, a)Bulk density – HHV, b)Bulk density – Cold gas efficiency, c)Bulk density – Carbon conversion efficiency, d)Bulk density – CO/CO2, e)Bulk density – Mass conversion factor, f)Bulk density – specific energy rate, g)Bulk density – gasification rate

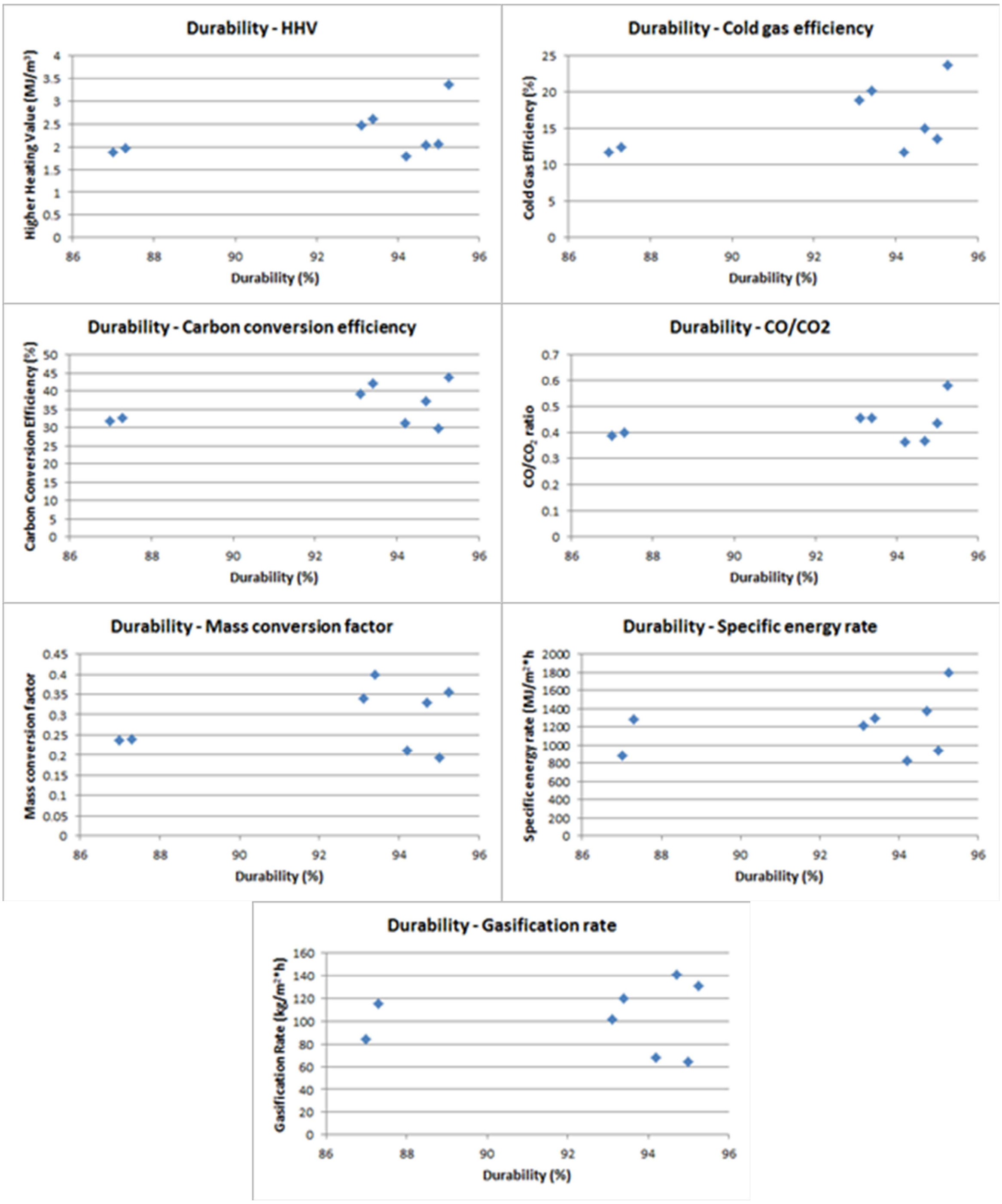

Figure 6.26: Relationship of the pellet durability with the gasification quality parameters, a)Pellet durability – HHV, b)Pellet durability – Cold gas efficiency, c)Pellet durability – Carbon conversion efficiency, d)Pellet durability – CO/CO2, e)Pellet durability – Mass conversion factor, f)Pellet durability – specific energy rate, g) Pellet durability – gasification rate

In the case of the relationship of durability with the gasification parameters (Figure 6.26), the trend once again seems positive in the case of 5 mm pellets (except for the cases of specific energy rate and gasification rate) and unclear in the case of the 18 mm pellets. In addition, the trend in the case of spouted fluidised bed gasification seems similar to the one of the downdraft gasification (see section 6.1.3) but perhaps for different reasons that will be discussed. There is an important difference though. In downdraft gasification, the relationship of durability with specific energy rate and gasification rate is clear in the case of 5 mm pellets but it is not clear in the spouted fluidised bed gasification.

6.2.4 Effect of pelleting parameters on the spouted fluidised bed gasification process

In this section the effect of the initial pelleting parameters on the gasification parameters is presented. Again, type 8 is considered as a co-gasification test of a mixture of 50% OSRS pellets and 50% E-On Miscanthus pellets. Thus, the basic comparison will be conducted using the first three pairs in the graphs to follow.

The first set of graphs is shown in Figure 6.27 and represents the effect of feedstock moisture content on the spout bed gasification parameters. In the cases of the effect of feedstock moisture content on the HHV, the cold gas efficiency, the carbon conversion efficiency and the mass conversion factor, the trend is quite clear. The lower the feedstock moisture content, the higher the values are. The effect loses its weight in the case of the CO/CO_2 ratio, possibly because there are many other factors affecting this trend too, such as the input condition parameters (even though the ER is similar). The last observation is possibly valid in the case of specific energy rate and gasification rate. Thus there is also an effect of the initial condition parameters (biomass, air feed) even when the ER is the same. Furthermore, type 8 test had higher values in nearly all cases, except in the case of mass conversion factor.

The second set of graphs is shown in Figure 6.28 and represents the effect of feedstock particle size upon the spout bed gasification parameters. It appears that there are minor differences between pairs with different feedstock particle size even though every other parameter is the same, even the initial condition parameters. In most of the cases, the differences are only minor, which it means that feedstock particle does play a minor role in the spout bed gasification, something that could not be observed in the case of downdraft gasification. The major differences between the pairs are caused by the differences in the initial condition parameters, even though the ER is the same.

The third set of graphs is shown in Figure 6.29 and represents the effect of die diameter upon the spouted fluidised bed gasification parameters. In most of the cases it is clear that the smaller the size of the pellet is, the higher the values are in each specific graph with the exception of the specific energy rate and gasification rate. The possible reasons are mentioned before: the two latter ratios are highly affected by the initial condition parameters, even with similar ER.

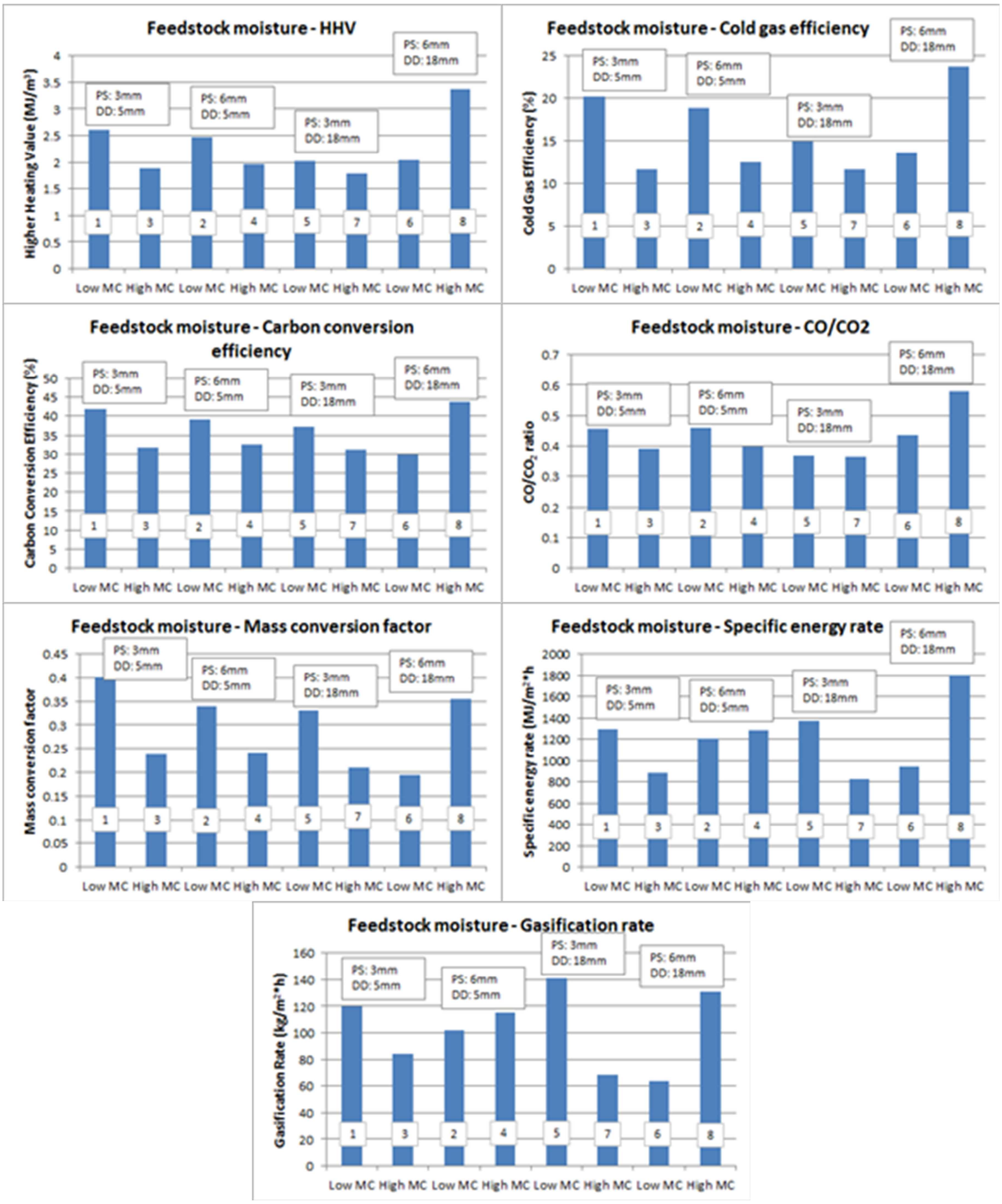

Figure 6.27: Effect of feedstock moisture content on the gasification quality parameters, a)Feedstock moisture – HHV, b)Feedstock moisture – Cold gas efficiency, c)Feedstock moisture – Carbon conversion efficiency, d)Feedstock moisture – CO/CO2, e)Feedstock moisture – Mass conversion factor, f)Feedstock moisture – specific energy rate, g)Feedstock moisture – gasification rate

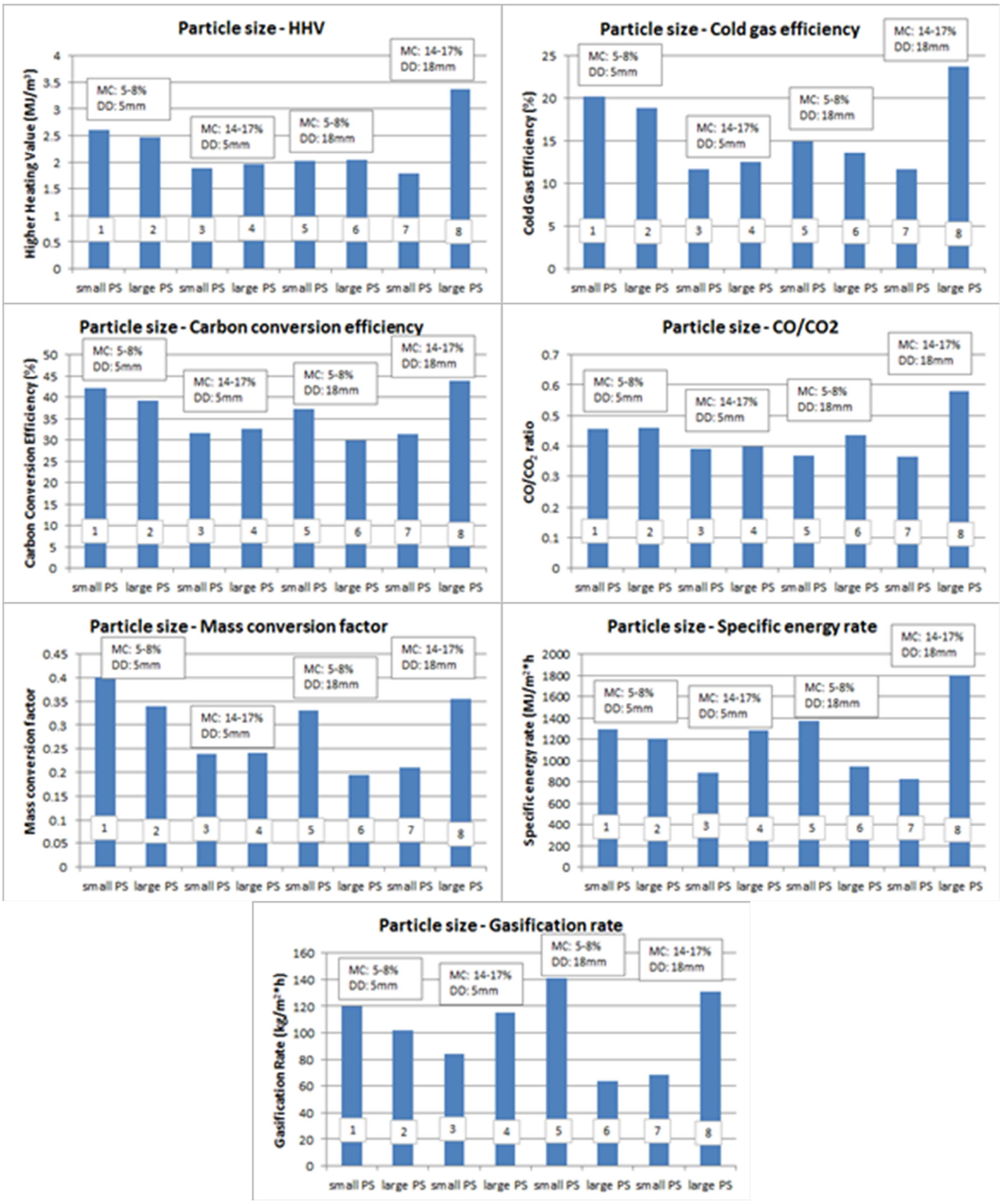

Figure 6.28: Effect of feedstock particle size on the gasification quality parameters, a)Feedstock size – HHV, b)Feedstock size – Cold gas efficiency, c)Feedstock size – Carbon conversion efficiency, d)Feedstock size – CO/CO2, e)Feedstock size – Mass conversion factor, f)Feedstock size – specific energy rate, g)Feedstock size – gasification rate

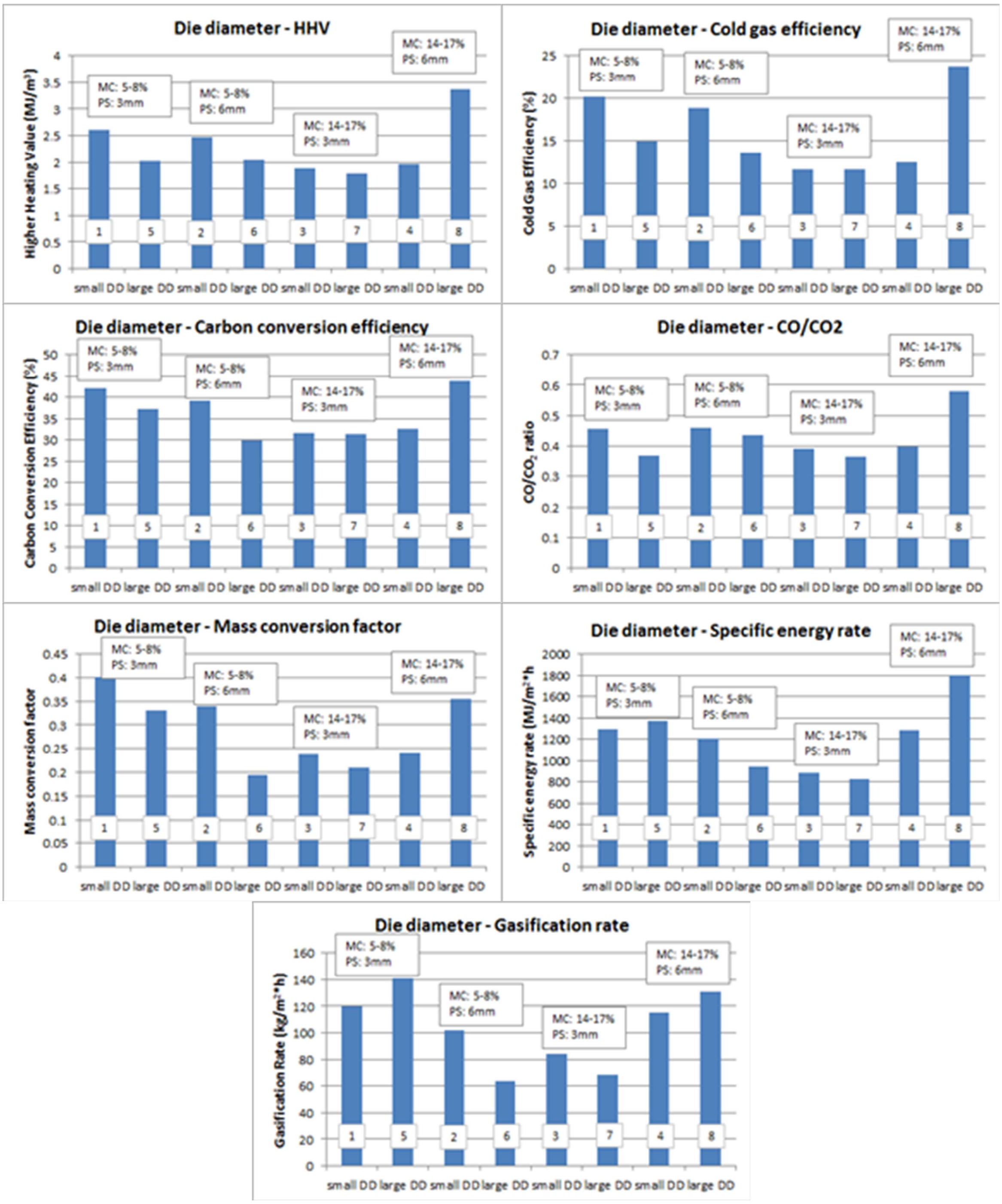

Figure 6.29: Effect die diameter on the gasification quality parameters, a)Die diameter – HHV, b)Die diameter – Cold gas efficiency, c)Die diameter – Carbon conversion efficiency, d)Die diameter – CO/CO2, e)Die diameter – Mass conversion factor, f)Die diameter – specific energy rate, g)Die diameter – gasification rate

6.2.5 Discussion

The spout bed technique was presented by Mathur and Gishler [135] as far back as the year 1955, but not as a thermal conversion technique. Still today there is not much experience on gasification in a spouted fluidised bed. A comparison of a fluidising bed and spouted fluidised bed in the gasification process by Hoque *et al* [136], showed a minor difference in the gas quality between the spout and the fluid bed. Thus, in the discussion that follows is prudent to also use fluid bed cases from the literature.

Concerning the effect of the feedstock moisture content on the gasification parameters, similar trends with the downdraft gasification case, were observed. The pellets that were manufactured from the dry feedstock resulted in higher gasification efficiency.

As in the downdraft gasification case, the feedstock moisture content affected not only the pellet moisture content but a series of parameters that were explained (see section 6.1.5). In general increasing the moisture content, the CH_4, CO and heating value is decreasing and the CO_2, H_2 increasing due to the energy dissipation for the evaporation of moisture. Despite that, higher amount of H_2 is gained through that energy dissipation [137]. The latter could not be confirmed from our experiments since the H_2 in the syngas was not higher in the case of the wet pellets. There are other authors that have investigated the topic. Sanz and Corella [138], using a model for a circulating fluid bed gasifier, showed that an increase in moisture content resulted in an increase of CO_2, H_2 and H_2O while the CO decreased. They also show that the CH_4 also increases with increasing moisture but only for ER values of 0.3 and above and the lower heating value slightly decreases but the latter is compensated by an increase of the gas yield.

The feedstock particle size did not seem to have any effect on the gasification process but on the other hand the size of the pellets did have an effect. The smaller size of biomass particle is generally related to the increased particle surface area over the volume ratio which leads to a higher syngas quality. Hernandez *et al* [139] conducted tests in an entrained flow gasifier and concluded that an increase of the size of the biomass material from 0.5-8 mm will decrease the percentage of CO, H_2 and CH_4 and will increase the amount of CO_2. Furthermore they concluded that with the increase of particle size there is a decline of the lower heating value of the gas, the mass conversion, as well as a decline of the cold gas efficiency. In addition, the gas yield remains fairly constant in the entire range of sizes. As it was expected, the smaller the particle size, the more efficient the heat transfer due to the increased particle surface area over volume. Thus the char is always expected to be more porous due to the higher volatile release which leads to an increase of the reactivity which in turn leads to a higher number of gasification reactions. This was also discussed in the previous chapter (see section 6.1.5), in the case of the downdraft gasification where the same phenomenon took place and is reported by many authors in the literature. If a small particle is pyrolysed, the reactivity of its char is higher than if a larger particle is pyrolysed and the time that is necessary for a large particle to achieve a specific conversion level also increases [140, 141]. Furthermore, the larger the particle, the greater the heat resistance is. As the particle size increases from fine to about 1 mm the kinetic control gives way to diffusion and heat transfer control [142, 100]. Thus, diffusion control dictates the process for both sizes of pellets 5 mm and 18 mm but this is not followed by pellets with the lower durability due to the higher amount of fines that are formed.

The char yield increases with particle diameter up to the 4 mm size, due to the fact that the temperature progresses slower inside large particles [143]. In one more study, it is concluded that the pyrolysis process is highly dependent on the heating rate. Furthermore, the larger the particles (up to a point) the slower is the heating rate and thus the pyrolysis conditions are changing [144]. The differences in the size also connected with the ash behaviour; in general the fines and coarse particles tend to yield lesser amount of alkalis in comparison to the larger particles [145]. So, it is possible that fines formed from pellets with low durability have lesser amount of alkalis than the pellets themselves and thus the catalytic effect of the ash in these fines is decreased. Furthermore, the smaller the particle size (in range of 0.2-0.8 mm) the higher the percentage of CO, CH_4, heating value, carbon conversion efficiency and the smaller the CO_2 [100]. Thus we can conclude that the fines from the pellets with lower durability will exhibit different behaviour from the pellets themselves. Especially in the case of the spout bed, the intense mixing could cause the entrainment of the char particles with the flow and thus decrease the gasification behaviour.

6.3 Gasification of other biomass

In this section the results of the downdraft and spouted fluidised bed gasification of other biomass feeds that were used throughout the course of this project are presented and discussed. The biomass feeds are the E-On Miscanthus pellets, DDGS pellets and oilseed rapes straw as used in the downdraft gasifier and the E-On Miscanthus pellets as were used in the spouted fluidised bed gasifier. The presentation of the feeds is followed by an overall comparison between all the feeds for both gasifiers and a discussion and comparison with results taken from the literature.

6.3.1 Downdraft gasification of Miscanthus pellets

In this subchapter the gasification of E-On Miscanthus pellets and their utilization in a downdraft gasifier is presented. In Table 6.6 results presented for escalating equivalence ratio in the range of 0.25-0.42.

Table 6.6: Performance of the E-On Miscanthus pellets in a downdraft gasifier with escalating ER range: 0.25-0.42

		E-On Miscanthus pellets test No								
		1	2	3	4	**5**	6	7	8	9
Biomass feed (kg/h)		9	8	9.5	8.3	8.3	7.65	8.2	8.2	8.3
Air feed (l/min)		150(1)	140(2)	160(3)	180(4)	200(5)	200(5)	220(6)	230(7)	240(8)
Equivalence ratio		0.25	0.26	0.26	0.32	0.35	0.38	0.39	0.41	0.42
Average gas composition	CO	10.47	10	14.26	14.55	15.5	15.52	14.7	15.5	15.1
	CO_2	6.45	11.4	12.07	13.7	14	11.38	12.7	13.6	13.6
	H_2	5.1	6.25	11.29	7.6	12	11.1	9	12.2	11.5
	CH_4	1.66	1.4	1.93	1.7	1.6	1.57	1.6	1.5	1.34
	N_2	76.32	70.95	60.45	62.45	56.9	60.43	62	57.2	58.46
Gas yield ($m^3/kg_{biomass}$)		1.35	1.17	1.33	1.65	2.02	2.06	2.06	2.34	2.36
HHV (MJ/m^3)		2.6	2.6	4	3.5	4.125	4	3.65	4.1	3.9
Cold gas efficiency (%)		19	16.4	28.2	30.9	42	43.9	40.1	51	49
Carbon conversion efficiency (%)		30	32	45	60	75	70.5	72	86	85
CO/CO_2 ratio		1.62	0.877	1.18	1.062	1.107	1.36	1.157	1.139	1.11
Mass conversion factor		0.071	0.12	0.29	0.4	0.58	0.448	0.47	0.64	0.62
Specific energy rate (MJ/m^2*h)		705	545	1117	1057	1526	1394	1360	1740	1688
Gasification rate (kg/m^2*h)		13.7	20	59	71	102	73.3	82	113	110

(1)Error: <5%, ±7.5 l/min
(2)Error: <5%, ±7 l/min
(3)Error: <5%, ±8 l/min
(4)Error: <5%, ±9 l/min
(5)Error: <5%, ±10 l/min
(6)Error: <5%, ±11 l/min
(7)Error: <5%, ±11.5 l/min
(8)Error: <5%, ±12 l/min

CO was in the range of 10-15% and the CO_2 in the range of 6-14%. H_2 lay within the range of 5.1-12.2% and CH_4 within the range of 1.34-1.93%. Gas yield also varied considerably and lay within the range of 1.17-2.36 m^3/kg while the heating value was relatively high for air gasification reaching values of 4.125 MJ/m^3 with a minimum value of 2.6 MJ/m^3. The cold gas and carbon conversion efficiencies lay within the range of 16.4-51% and 30-86% respectively. Good gasification performances could be observed in the higher equivalence ratios.

The graphical representation of the above can be observed in Figure 6.30 where a set of graphs is presenting the gasification of Miscanthus pellets within the ER of 0.25-0.42. The gasification parameters of cold gas efficiency, carbon conversion efficiency, mass conversion factor, specific energy rate and gasification rate seems to have an positive correlation with the increasing equivalence ratio while the parameters of CO/CO_2 ratio and higher heating value the trend is quite unclear. Even so, a slightly positive trend of the heating value can be detected for an increasing equivalence ratio. This could be attributed to the slight decrease of CH_4 concentration in the higher equivalence ratios.

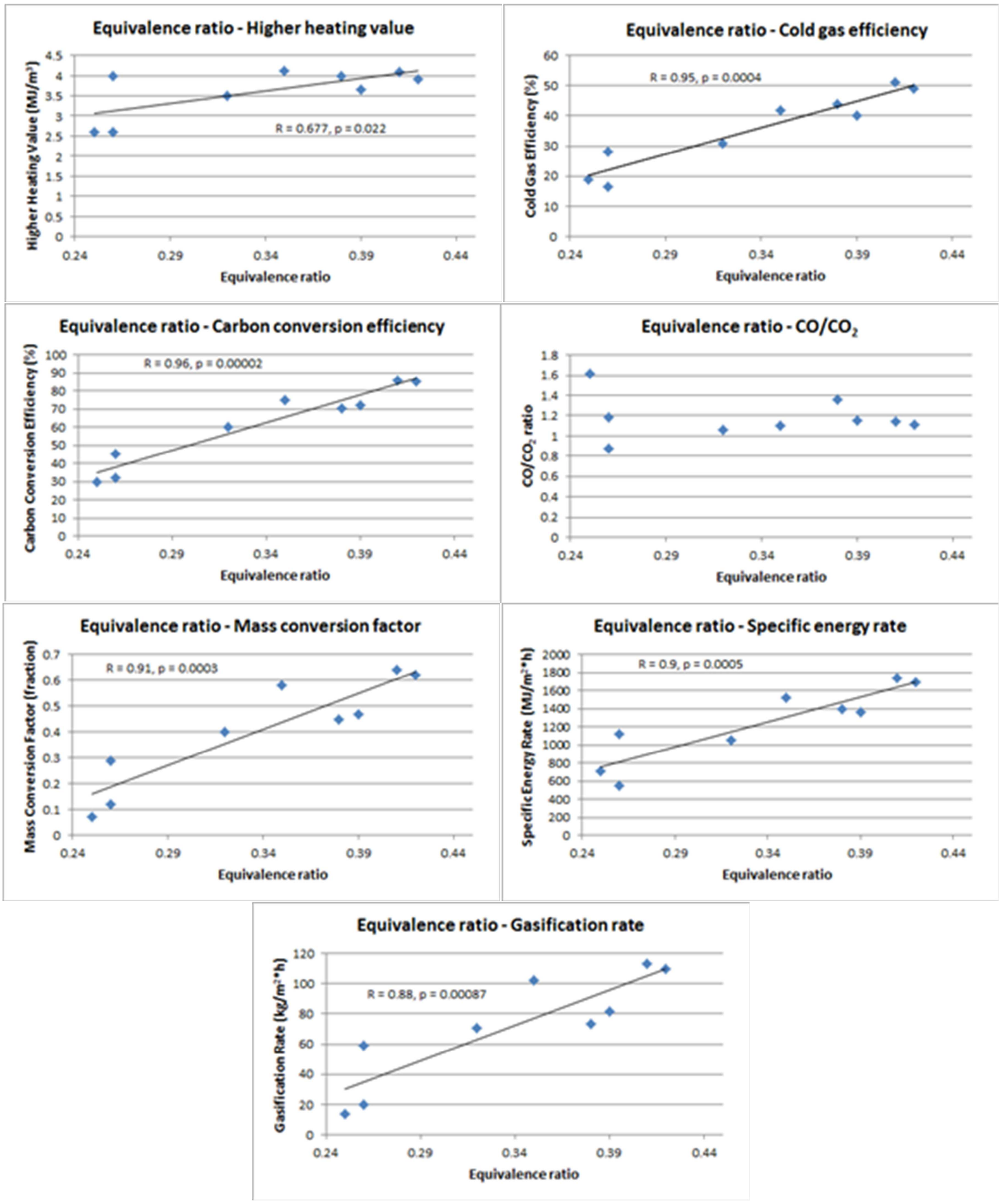

Figure 6.30: Relationship of equivalence ratio with the gasification quality parameters, Miscanthus pellets, downdraft, a)ER – HHV, b)ER – Cold gas efficiency, c)ER – Carbon conversion efficiency, d)ER – CO/CO2, e)ER – Mass conversion factor, f)ER – specific energy rate, g)ER – gasification rate

6.3.2 Downdraft gasification of DDGS pellets

In this subchapter the gasification of DDGS pellets and their utilization in a downdraft gasifier is presented. In Table 6.7 the results of the gasification performance are presented.

CO reaches 11.17% with a minimum value of 4.5% while CO_2 reaches 15.4% with a minimum value of 12.7%. H_2 has a maximum value of 5.59% and a minimum of 1.66 while CH_4 has a maximum value of 1.43% and a minimum of 0.8%. The gas yield lay within the range of 0.96-2.36 m^3/kg while the heating value lay within the range of 1.1-2.35 MJ/m^3. It is interesting to point out here that except for the ER value of 0.26 in all other cases either in high or low ER, the heating value was within the range of 2-2.6 MJ/m^3 which is a relatively small range of values. The cold gas and carbon conversion efficiencies lay within the values of 7.1-27.9% and 29.8-70% respectively.

Table 6.7: Performance of the DDGS pellets in a downdraft gasifier with escalating ER range: 0.2-0.47

		DDGS pellets test No					
		1	2	3	4	5	6
Biomass feed (kg/h)		9	7.6	8.3	4.5	8	4
Air feed (l/min)		130$^{(1)}$	120$^{(2)}$	160$^{(3)}$	90$^{(4)}$	170$^{(5)}$	140$^{(6)}$
Equivalence ratio		0.2	0.21	0.26	0.27	0.29	0.47
Average gas composition	CO	8.9	8.34	4.5	11.17	7.46	9.24
	CO_2	12.7	14.17	15.4	13.9	13.3	14.3
	H_2	5.5	5.59	1.66	4.8	4.54	4.76
	CH_4	1.3	1.22	0.8	1.43	1.21	1
	N_2	71.6	70.68	77.64	68.7	73.49	70.7
Gas yield ($m^3/kg_{biomass}$)		0.96	1.06	1.18	1.39	1.377	2.36
HHV (MJ/m^3)		2.35	2.25	1.1	2.6	2	2.17
Cold gas efficiency (%)		12.2	13	7.1	19.7	15	27.9
Carbon conversion efficiency (%)		26.7	30.6	29.8	44.5	36.7	70
CO/CO_2 ratio		0.7	0.588	0.29	0.8	0.56	0.65
Mass conversion factor		0.11	0.152	0.097	0.26	0.137	0.366
Specific energy rate (MJ/m^2*h)		448	402	239	357	489	452
Gasification rate (kg/m^2*h)		20.1	23.1	16.1	23	21.8	29.3

(1)Error: <5%, ±6.5 l/min
(2)Error: <5%, ±6 l/min
(3)Error: <5%, ±8 l/min
(4)Error: <5%, ±4.5 l/min
(5)Error: <5%, ±8.5 l/min
(6)Error: <5%, ±7 l/min

A graphical representation of the downdraft gasification process of the DDGS pellets is shown in Figure 6.31. In most cases the effect of the equivalence ratio is not certain or clear. However if one does not add the results for ER: 0.26, then some interesting effects can be observed. The cold gas efficiency and carbon conversion efficiencies have a positive correlation within the escalating ER range. The higher heating value, the CO/CO_2 ratio and the specific energy rate does not seem to follow similar trends within the same ER range. On the other hand the mass conversion factor and the gasification rate seem to have a positive correlation within the ER range without this correlation being very clear. The gasification of

DDGS pellets it general showed lower efficiencies in comparison to the other biomass feeds due to the implications that the ash has caused. The latter will be discussed in following chapters.

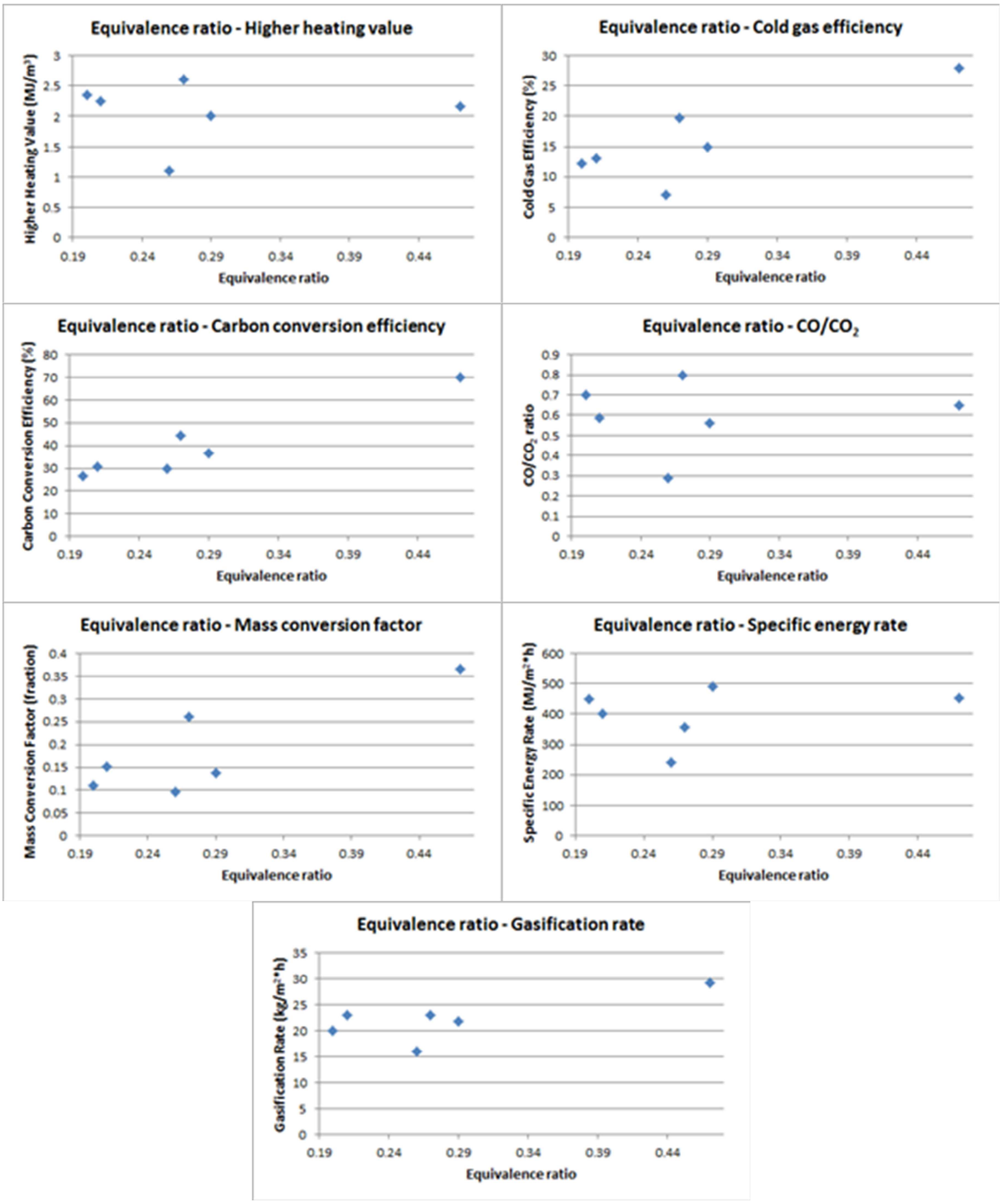

Figure 6.31: Relationship of equivalence ratio with the gasification quality parameters, DDGS pellets, downdraft, a)ER – HHV, b)ER – Cold gas efficiency, c)ER – Carbon conversion efficiency, d)ER – CO/CO2, e)ER – Mass conversion factor, f)ER – specific energy rate, g)ER – gasification rate

6.3.3 Downdraft gasification of oilseed rape straw

In this subchapter, the gasification of oilseed rape straw and its utilization in a downdraft gasifier is presented. Generally speaking, the gasification of the oilseed rape straw was very difficult to control. One of the difficulties was the frequent feeding of the gasifier since the gasifier itself has to be fed in batches and the conversion rate of the straw was extremely rapid due to the lower density of the fuel. An effort was made to keep similar initial input conditions but it was proved difficult. In Table 6.8 the results of the test are shown.

Table 6.8: Performance of loose oilseed rape straw in a downdraft gasifier in two equivalence ratios 0.5 and 0.84

		Oilseed rape straw	
		1	2
Biomass feed (kg/h)		6	6
Air feed (l/min)		180(1)	300(2)
Equivalence ratio		0.5	0.84
Average gas composition	CO	6.7	10.3
	CO_2	15.6	11.5
	H_2	4.5	3.96
	CH_4	1.33	0.46
	N_2	71.87	73.78
Gas yield ($m^3/kg_{biomass}$)		1.99	3.23
HHV (MJ/m^3)		1.95	1.99
Cold gas efficiency (%)		24	41
Carbon conversion efficiency (%)		62	94
CO/CO_2 ratio		0.43	0.9
Mass conversion factor		0.28	0.28
Specific energy rate (MJ/m^2*h)		514	851
Gasification rate (kg/m^2*h)		35	35

(1)Error: <5%, ±9 l/min
(2)Error: <5%, ±15 l/min

In all cases the gasification of oilseed rape straw showed lower values than the gasification of its pellets except in terms of cold gas end carbon conversion efficiencies (see sections 6.2.1 and 6.2.2). That is possibly because of the lower energy and bulk density of the fuel. Furthermore the consumption of feed was also lower despite keeping the initial air feed in similar ranges as the gasification of OSRS pellets. This is due to the low bulk density of the straw and also because of the frequent feeding of the gasifier. The experiments for both the pellets and the straw it should be repeated in a continuous fed downdraft gasifier so that the differences in the phenomena that occurred can be clearly understood.

6.3.4 Spouted fluidised bed gasification of Miscanthus pellets

In this subchapter the gasification of E-On Miscanthus pellets and its utilization in a spout bed gasifier is presented. It's prudent to say that all gasification experiments are unique and it is very difficult to receive the exact same results even with the same input. An example is given in Appendix C where data fluctuations are quite large even though the exact same initial operating conditions are used. But nevertheless, despite the differences, a similar pattern is always followed.

In Table 6.9 the performance of E-On Miscanthus pellets with escalating ER is shown. The ER range under consideration is 0.19-0.39. CO lay within the range of 14.05-17% while CO_2 lay within the range of 13.2-16.1%. H_2 reaches as high as 14% with a minimum value of 9% while CH_4 reaches the value of 4.5% having a minimum value of 2.7%. The gas yield also varies from 1.22 m^3/kg to 2.17 m^3/kg while the higher heating value which is among the highest observed among all the gasification tests, varies from 4-5.53%. Cold gas and carbon conversion efficiencies, which were also among the highest of all gasification tests, lay with the range of 35.5-50.8% and 53-85.1% respectively. It is interesting to see that the highest performances, in terms of heating value, was observed at the lowest values of equivalence ratio in which the effect of all the reduction reactions was enhanced. Even though the gas yield is lower (at the low ERs), the heating value is high enough to compensate for this and has greater values of gasification rate than in the case of high ER values. This is likely to be due to the effect of water gas shift reaction which its equilibrium is shifted towards the production of H_2 and also the methanation reaction that used the H_2 to produce CH_4.

Table 6.9: Performance of the E-On Miscanthus pellets in a spouted fluidised bed gasifier with escalating ER range: 0.19-0.39

		E-On Miscanthus pellets with escalating ER							
		1	2	3	4	5	6	7	8
Biomass feed (kg/h)		11.7(4)	9.5(3)	7.6(1)	7.3(1)	7.6(1)	6(2)	7.6(1)	7.6(1)
Air feed (l/min)		150(5)	150(5)	150(5)	150(5)	175(6)	150(5)	200(7)	205(8)
Equivalence ratio		0.19	0.23	0.29	0.3	0.34	0.37	0.38	0.39
Average gas composition	CO	15.5	15.95	16.9	17	16.1	14.05	15.2	14.85
	CO_2	16.1	15	13.2	13.5	13.5	14	14.3	14
	H_2	14	12.7	11.7	12.2	10.5	9	9.7	9
	CH_4	4.5	4.1	3.4	3.87	3.2	2.7	3.1	3
	N_2	49.9	52.25	54.8	53.43	56.7	60.25	57.7	59.15
Gas yield ($m^3/kg_{biomass}$)		1.22	1.44	1.7	1.83	1.93	1.98	2.17	2.17
HHV (MJ/m^3)		5.53	5.27	5	5.24	4.65	4	4.4	4.2
Cold gas efficiency (%)		35.5	40	45.3	50.8	47.7	42	50.7	48.7
Carbon conversion efficiency (%)		53	60.6	69	75.6	76.2	73	85.1	83.1
CO/CO_2 ratio		0.96	1.06	1.28	1.26	1.19	1	1.06	1.06
Mass conversion factor		0.463	0.5	0.529	0.595	0.569	0.51	0.637	0.6
Specific energy rate (MJ/m^2*h)		4424	4021	3625	3915	3814	2646	4047	3888
Gasification rate (kg/m^2*h)		293	257	217	235	233	166	261	246

(1)Error (SD): ±0.403kg
(2)Error (SD): ±0.375kg
(3)Error (SD): ±0.376kg
(4)Error (SD): ±0.562kg
(5)Error: <5%, ±7.5 l/min
(6)Error: <5%, ±8.75 l/min
(7)Error: <5%, ±10 l/min
(8)Error: <5%, ±10.25 l/min

In Figure 6.32, the performance of spout bed gasification of E-On Miscanthus pellets is illustrated. The cold gas efficiency, the carbon conversion efficiency and the mass conversion factor show an increasing pattern with increasing equivalence ratio. This is due to the decrease of fuel/air ratio, thus there is more air to react with the fuel. The higher heating value, on the contrary, shows a decreasing pattern with increasing equivalence ratio due to the reasons mentioned in the previous paragraph. The ratio of CO/CO_2 is increasing and at the ER value of 0.3 it starts decreasing. This is happening due to the enhanced effect of Boudouard reaction because of the increased temperature. The increase of air supply perhaps increasing the temperature even more but also increases the CO_2 percentage even more and thus the 0.3 value of ER is the threshold between a high and low effect of the Boudouard reaction. The specific energy rate and the gasification rate seem to decrease up to ER value of 0.3 and then start increasing thereafter. Since specific energy rate depends on the gas flow rate (connected with the gas yield) and the higher heating value of the gas the pattern shifts slightly to increasing energy rate with ER because the gas flow rate is increasing also. Similar is the reason that applies to the gasification rate. The threshold it seems ones more to be the ER value of 0.3.

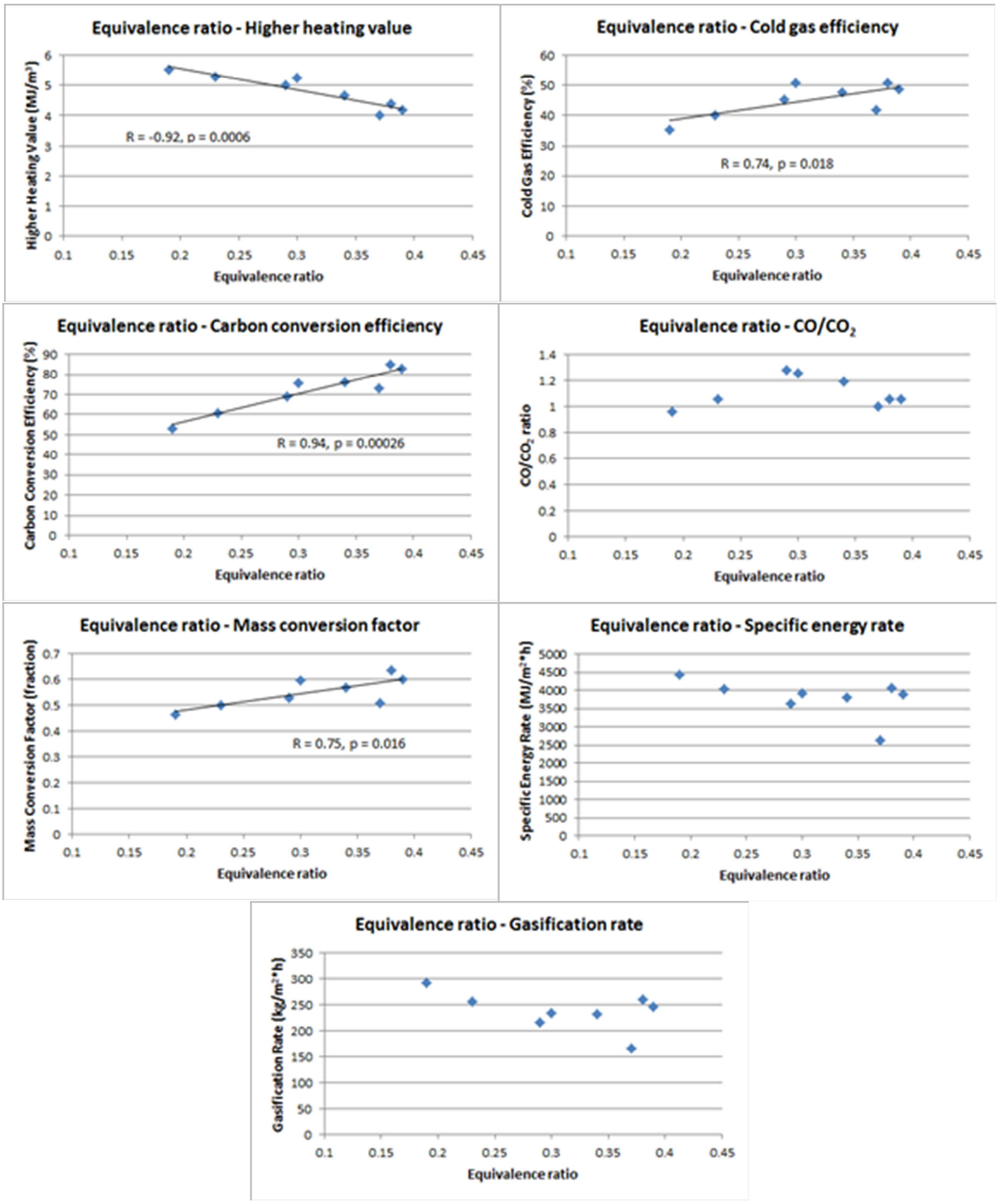

Figure 6.32: Correlation of equivalence ratio with the gasification quality parameters, a)ER – HHV, b)ER – Cold gas efficiency, c)ER – Carbon conversion efficiency, d)ER – CO/CO2, e)ER – Mass conversion factor, f)ER – specific energy rate, g)ER – gasification rate

6.3.5 A comparison between OSRS and other biomass pellets

In this subchapter a comparison between OSRS pellets, Miscanthus pellets and DDGS pellets is presented for both cases, downdraft and spout bed. In the first section a comparison between the OSRS pellets, the Miscanthus pellets and the DDGS pellets for downdraft gasification is presented while in the second section the comparison between the OSRS pellets, the co-gasification case and the Miscanthus pellets for spout bed gasification is highlighted. In the third section of this subchapter the case of the spout bed de-fluidization is showed followed by the last section in which a discussion is made and a comparison with other results from literature.

Downdraft gasification

In Figure 6.33 a set of graphs is shown that represent a comparison of the pellets tested in the downdraft gasifier in terms of their gasification quality results. In nearly all cases the same pattern is followed. Miscanthus pellets show the highest values in all cases followed by the dry (type 1 and 2) OSRS pellets, the wet (type 3 and 4) OSRS pellets and finally the DDGS pellets. The case of type 5-type 8 OSRS pellets is meaningful only in the case of carbon conversion efficiency.

Since the size of all types of pellets has small differences, their differences in the behaviour cannot be attributed in the size. Instead the greatest effect perhaps is the catalytic behaviour of the ash for the different fuels. This is going to be discussed in the last section of this subchapter.

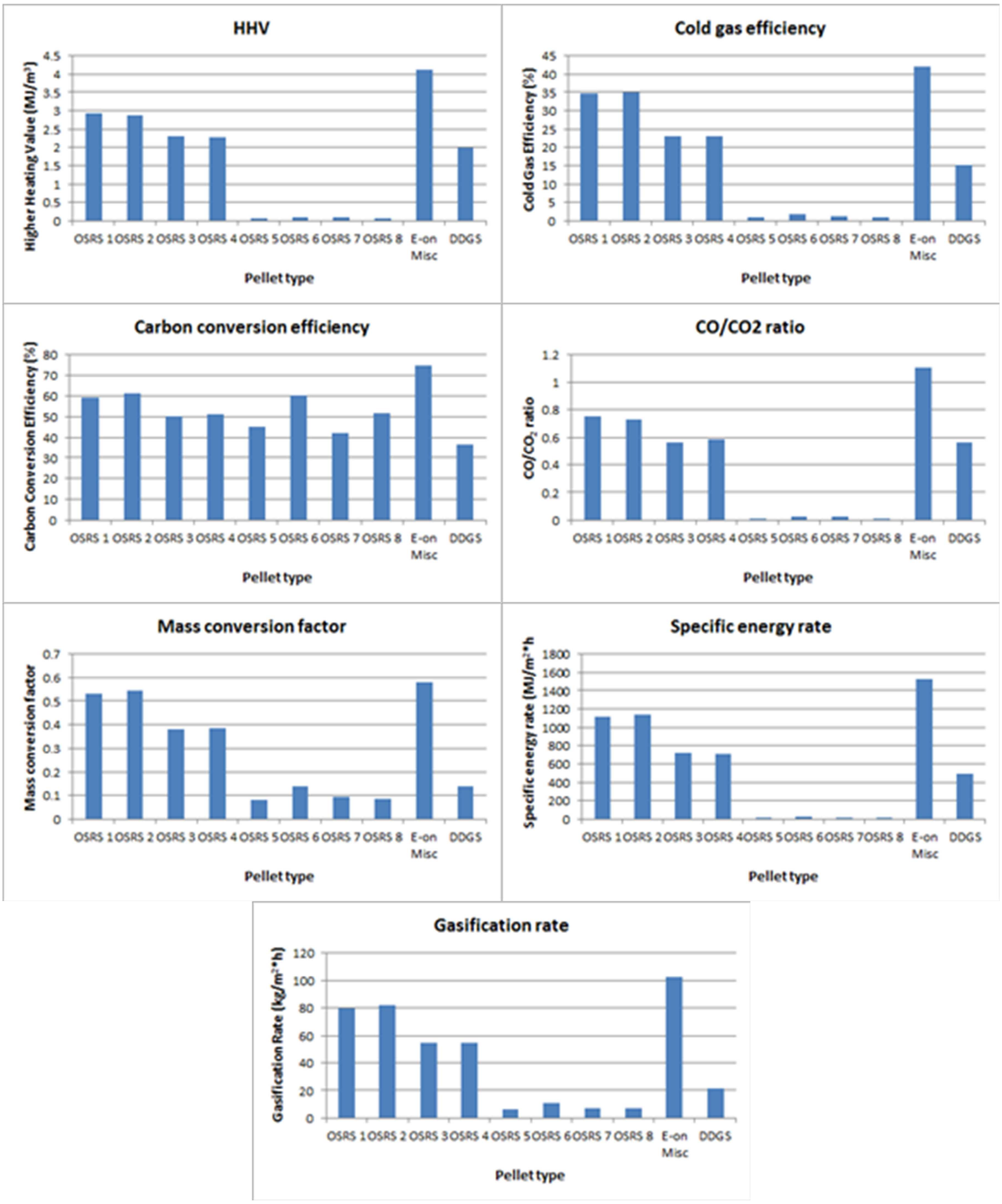

Figure 6.33: Comparison of tested pellets in terms of their downdraft gasification quality, a)HHV, b)Cold gas efficiency, c)Carbon conversion efficiency, d)CO/CO2, e)Mass conversion factor, f)specific energy rate, g)gasification rate

Spouted fluidised bed gasification

Figure 6.34 shows a set of graphs that represent a comparison of the pellets tested in the spout bed gasifier in terms of their gasification quality results. The fuels tested in the spout bed gasifier are the OSRS pellets the Miscanthus pellets and a 50-50% co-gasification case. The Miscanthus pellets show the highest values in the gasification performance followed in the most of the cases by the co-gasification of type 8 OSRS pellets with Miscanthus pellets, the dry small size OSRS pellets, the wet small size OSRS pellets and finally the large size pellets. It seems also, that there are cases that the large pellets have higher values than the wet small size pellets.

There are also few cases that the latter generalization does not apply such as the case of gasification rate of the type 5 OSRS pellets. The value of gasification rate of the type 5 OSRS pellets is higher even if it is compared with the co-gasification case. It is prudent to restate the previous conclusion that the spout bed gasifier's performance is highly affected by the initial operating conditions even in cases in which the ER is exactly the same.

Furthermore, an interesting observation is the small differences between the small and large OSRS pellets but the huge difference of the two latter with the performance of Miscanthus pellets. This is an indication that, in the case of spout bed gasification, the chemical characteristics has a higher weight than the physical characteristics of the pellets. This is going to be discussed in the last section of this subchapter.

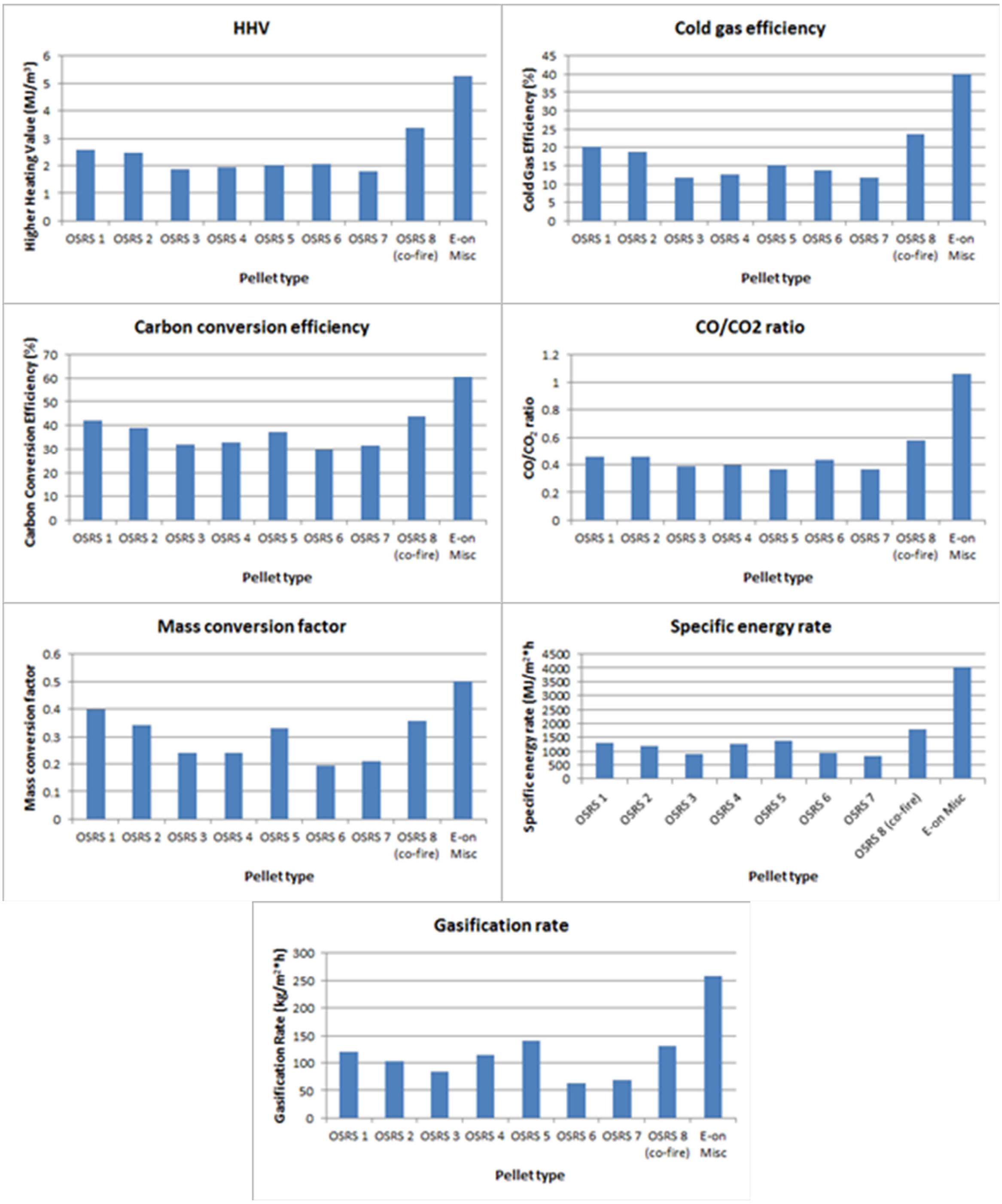

Figure 6.34: Comparison of tested pellets in terms of their spouted fluidised bed gasification quality, a)HHV, b)Cold gas efficiency, c)Carbon conversion efficiency, d)CO/CO2, e)Mass conversion factor, f)specific energy rate, g)gasification rate

Bed de-fluidization

In the current section a presentation of the de-fluidization case is made. Unlike the E-On Miscanthus pellets that were not responsible for the spout bed de-fluidization even in high temperatures, the case was not the same for the oilseed rape straw pellets. It was found that during the gasification of OSRS pellets the bed de-fluidizes at 850^{o}C. This phenomenon is shown in Figure 6.35 in which, at the point of 850^{o}C, a destabilization occurs and the temperatures represented by the thermocouples within the bed are breaking apart. This means that the bed is not fluidizing any more.

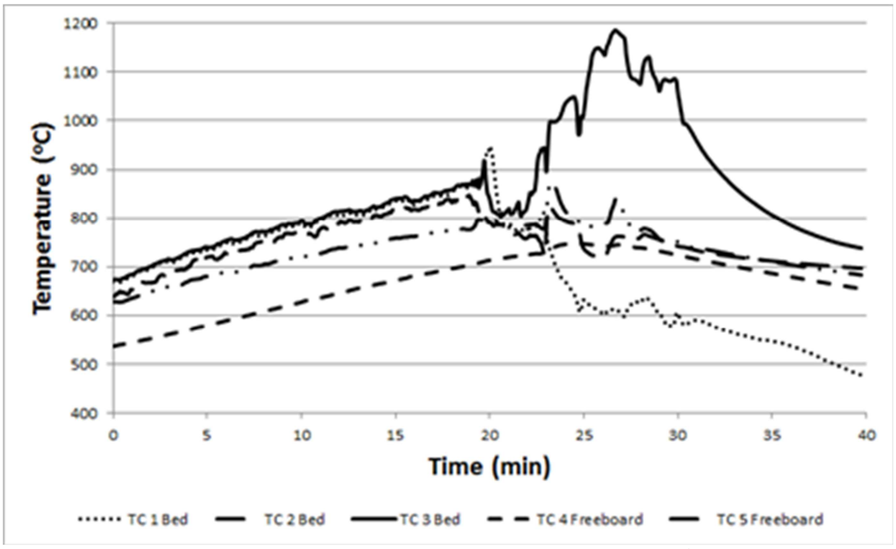

Figure 6.35: Bed de-fluidization at 850^{o}C

Table 6.10: Analysis of sieved material of bed after a Miscanthus pellets test, Figure 6.36, Picture b

Spectrum	O	Mg	Al	Si	P	S	K	Ca	Cr	Mn	Fe	Total
Analysis	46.08	1.82	1.79	9.74	3.79	0.58	4.45	25.77	0.81	0.51	4.66	100.00

Table 6.11: Analysis of sieved material after a successful OSRS pellets test (type 1)

Spectrum	O	Mg	Si	P	S	Cl	K	Ca	Fe	Br	Total
Analysis	50.79	1.15	26.06	0.54	0.55	0.96	12.66	5.07	1.05	1.18	100.00

Table 6.12: Analysis of sieved material after bed de-fluidization case (type 1), Figure 6.36, Picture a

Spectrum	O	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Total
Analysis	48.14	1.34	1.84	25.72	0.81	0.74	1.14	13.29	5.98	1.01	100.00

Table 6.13: Analysis of crystal form white sinter during de-fluidization case, Figure 6.37, Picture a

Spectrum	O	Mg	Si	K	Ca	Br	Total
Spectrum 1	55.59	0.42	38.64	3.46	1.15	0.74	100.00

Table 6.14: Analysis of brown agglomerated dry pulp during de-fluidization case, Figure 6.37, Picture b

Spectrum	O	Na	Mg	Al	Si	S	K	Ca	Ti	Fe	Total
Spectrum 1	50.18	1.93	2.00	8.27	21.86	0.92	3.60	6.16	0.52	4.56	100.00

In Tables 6.10-6.14, the SEM-EDS analysis of various ash samples is presented. Table 6.10 shows an ash sample taken from the sieved bed after a successful E-On Miscanthus test. The most characteristic species of the sample are the quite low amount of Si, the high amount of Ca and the low amount of K. An analysis of the ash taken from the sieved bed after a successful OSRS test is shown in Table 6.11. In this case and in comparison with the previous analysis there is a much higher percentage of Si, 26% over 9.7% in Miscanthus case, a much lower percentage of Ca, 5% over 25.5% in Miscanthus case, and a higher percentage of K, 12.7% over 4.4% in Miscanthus case. Nevertheless the temperature of the OSRS test was kept below the 800^{o}C and thus no de-fluidization had occurred.

Table 6.12 shows an ash sample taken from the sieved bed after its de-fluidization. As it can be observed, the ash analysis is very similar to the analysis of the successful OSRS test with the only exception of the appearance of small amounts of Al. Thus, it is most probable that the inorganic material is there during the entire test but once the temperature reaches 850^{o}C the inorganic material is re-organised and new species are formed that lead to the de-fluidization. It is possible that the 850^{o}C is the melting temperature of this specific combination of inorganic species that became sticky at that temperature.

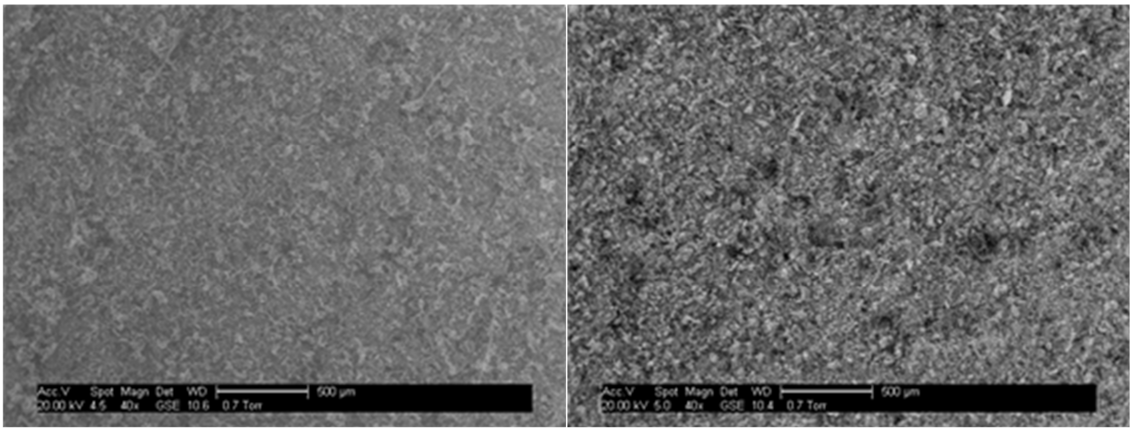

Figure 6.36: SEM pictures of sieved bed ash of ‘a’: OSRS pellets (de-fluidized) and ‘b’:Miscanthus pellets

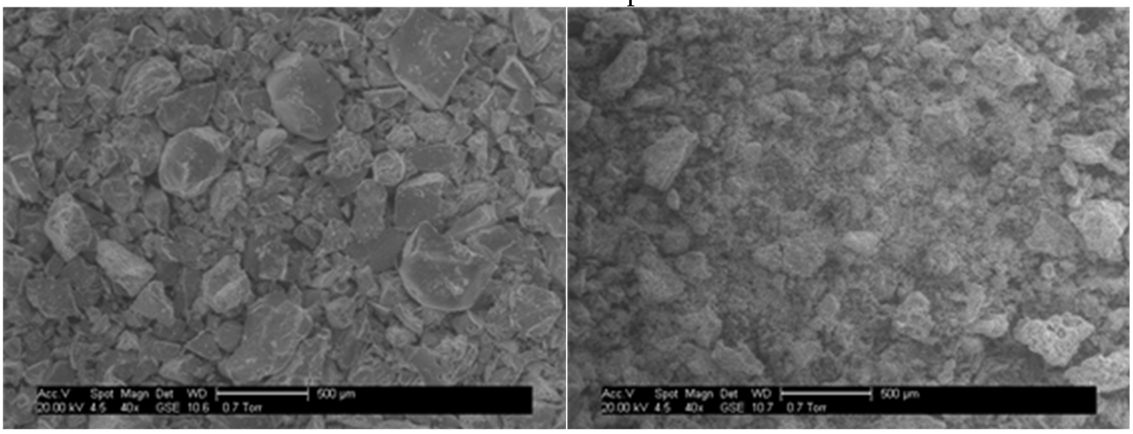

Figure 6.37: SEM pictures ‘a’ and ‘b’ of ash agglomerates formed during the bed de-fluidization in the OSRS type 1 test

Furthermore, the melting of the ash formed agglomerates, the analysis of these can be seen in Tables 6.13 and 6.14. One of the agglomerates was of crystal form and the analysis is shown in Table 6.13. This agglomerate is a silica based crystal possibly combined in various ways with oxygen. In Table 6.14 the second type of agglomerate that was observed is shown. The characteristic species are the increased amount of Fe and Na, lower percentage of Si and increased percentage of Ca in comparison to the previous agglomerate. The ash behaviour is explained in the following section.

6.3.6 Discussion and comparison with results from literature

In the current section there will be a discussion on the phenomena concerning the differences between our own and various other biomass fuels from the literature as gasified also using alternative gasification techniques. The section closes with a discussion on the behaviour of the ash on the gasification process.

The equivalence ratio plays a major role in the gasification role as it was also seen in the cases of the Miscanthus and DDGS pellets thus a discussion on the effect of ER on the gasification process is imperative. Gas yield increases with increasing ER, while heating value decreases with increasing ER because of the higher percentage of CO_2, which in turn is because of combustion has enhanced contribution over gasification. Furthermore the dilution effect of N_2 could also contribute to the decrease of heating value with increasing ER. In addition, H_2 and CO decreases, while CO_2 increases with increasing ER [97, 146, 141].

Other studies also confirm the decrease of the H_2, CO, CH_4 with an increasing ER and the increase of gas yield and carbon conversion with the increase of ER. This is due to the reaction of the gasification products, char and tars with O_2 to form CO. This of course leads to the decrease of heating value with an increase of ER. The N_2 dilution effect is also mentioned. Furthermore they mention the observation of increase of gas yield but at the same time is compensated by a decline of the heating value with an increasing ER [147, 146, 148, 149, 150, 151, 152, 137, 138, 153]. Furthermore the carbon conversion efficiency increases with increasing equivalence ratio [146, 141]. In addition mass conversion and cold gas efficiency increase with the ER [154]. All these studies are in agreement with the results presented here. Furthermore experiments in a dual-distributor fluid bed gasifier revealed similar trends and had the best gasification behaviour at the ER of 0.25 [155]. A different study, concluded that the optimum ER was 0.23 (air-steam experiments in fluid bed) [100].

Heating rate has a strong effect on the production of char from biomass but this effect is smaller in the case of char that was produced from coal and that could be attributed to the cellulose content of biomass. At temperature less than 300^{o}C, the cellulose dehydrates; at over 300^{o}C the cellulose de-volatilizes. Thus with a high heating rate the residence time of biomass at temperatures below 300^{o}C is very small and less important. At this point the dehydration reactions have a very short time to occur and thus blocking the production of the less reactive anhydro-cellulose (higher char yield). On the contrary, the fast heating favours the depolymerization of cellulose and the production of volatiles [140]. Furthermore the reactivity of agricultural residues studied as the author states, are lower than the reactivity of wood which led to a higher production of char. That occurred most likely due to the pelletisation of agricultural residues that lead to lower reactivity while loose agricultural residues could give a higher amount of volatiles [140].

In general, high percentage of C and low percentage of O_2 in the fuel, low H/C ratio and high lignin content favours the high yield of char [140]. It is possible that the lignin content plays a major role in the gasification performance of a fuel. In the experimental procedure chapter we show that the lignin content of oilseed rape straw is 11.16% while the one of Miscanthus is 21% (taken from Phyllis database [156]) and the one of DDGS is 4.3% [157]. So, it seems that there is a correlation of the gasification behaviour and the lignin content of the fuel. Butterman *et al* [158] reported the lignin contents of beachgrass (12%), alfalfa (14%), poplar (24%) and Douglas fir (28%). The authors discovered that the low lignin fuels yielded higher gasification residues but lower char volumes in comparison to the high lignin fuels. Furthermore the high gasification residues were correlated with a high mineral content while high pyrolysis char residues were correlated with the high lignin content. A similar result was reported by Lv *et al* [159], who pointed out that the cellulose part of the fuel is responsible for the volatile matter but the lignin part of the fuel is responsible for the char. It is possible that, due to the lower lignin content, the lower amount of char in OSRS and DDGS pellets is also one of the factors that affected the gasification process because fewer char gasification reactions took place. Furthermore, DDGS and OSRS had ash composition with no enhanced catalytic behaviour, thus reducing even further the number of gasification reactions that took place. That was possibly one of the reasons why Miscanthus pellets were gasified successfully but OSRS and DDGS did not.

Ghani *et al* [160] reported the lower heating value of gas that was produced from the fluid bed gasification of coconut shell and palm kernel shell for different equivalence ratios. In the ER of 0.25 the LHV of coconut shell was 0.47 MJ/m^3 while the one of palm kernel shell was 3.4 MJ/m^3. In the ER of 0.2 the LHV of coconut shell was 0.19 MJ/m^3 while the one of the palm kernel shell was 2.8 MJ/m^3. It is clear that the gasification performance of coconut shell was extremely lower than the most of the cases of OSRS, Miscanthus and even DDGS gasification. On the other hand the gasification performance of palm kernel shell was comparable with the gasification of OSRS, slightly lesser quality of the Miscanthus pellets gasification and in many cases better quality than the downdraft gasification of DDGS pellets. The decreased performance of the gasification of coconut shell comes from the fact that the volatile matter of this biomass is nearly 30% while the amount of ash reaches 43%. Thus despite of the high fixed carbon 26%, due to the high ash content and low volatile matter the gasification quality was reduced. On the other hand, the palm kernel shell has volatile matter comparable with our biomass samples (72%), ash content similar to the OSRS pellets (9%) but higher than Miscanthus and DDGS pellets, and fixed carbon higher than all of our samples (18.5%). Thus the amount of fixed carbon plays a role in the gasification performance but in this case it was overwhelmed by the extremely high ash content of the coconut shell. This happened in this case too in which the dry OSRS pellets have higher fixed carbon than the wet OSRS pellets. It is therefore likely that this was one of the reasons that the dry OSRS pellets had better performance than the wet OSRS pellets. On the other hand, the DDGS pellets had higher fixed carbon than both the OSRS pellets and yet this did not result in better gasification. This means that the fixed carbon is not a quality indicator for the gasification performance but instead a combination of indicators should be preferred. Type and amount of ash and volatile matter play also a major role in the pyrolysis and gasification performance.

Rajvanshi [119] reports the gaseous species production and gas heating value in downdraft gasification as taken from various sources in the literature. The report shows a heating value for:

- charcoal 4.6 MJ/m^3
- wood 5 MJ/m^3
- wheat straw pellets 4.5 MJ/m^3
- pressed sugarcane 5.3 MJ/m^3
- pelleted rise hulls 3.25 MJ/m^3
- cubed cotton stalks 4.3 MJ/m^3
- coconut husks 5.8 MJ/m^3
- coconut shells 7.2 MJ/m^3

In this case the coconut shells have good gasification performance reaching high gas heating values. That is because, as the author also reports, in the case where the coconut shell ash content is 0.8%, which means that the fuel was cleaned out of ash. Thus the amount of ash plays an important role in the gasification performance.

In a different study, the authors tested three different biomass samples in a steam fed fluid bed gasifier. They found out that sawdust had better gasification performance than peanut shell which in turn had better performance than wheat straw. They attributed this to the increased amount of volatile matter in the sawdust and the lower amount of volatile in the other two biomasses. What is not mentioned is the difference that the material has in the ash content. The sawdust concentration of K_2O and CaO was 10.45% and 17.54%, the one of peanut shell was 16.84% and 10.78%, and the one of wheat straw was 15.58% and 8.33%.

Thus the K/Ca ratio was increasing from sawdust to peanut shell to wheat straw which as mentioned in the introduction of the current project, could explain the behaviour of the fuels. Furthermore, the Fe_2O_3 was increasing from sawdust to wheat straw [147].

Haykiri-Acma *et al* [161] concluded in the steam char gasification case the inherent biomass properties such as the ash and the fixed carbon play an important role in the gasification process. They showed that the char from olive refuse had the smallest reactivity among other biomass samples because the fixed carbon of olive refuse was the smallest one in comparison to the other biomass samples and that led to the small amounts of char yield after the pyrolysis process. In addition they found that olive refuse had the highest amount of ash (more inorganics – less organics) and that may led to the lower char porosity and active surface area thus reducing the reactivity of the fuel. This could be valid for this case especially of OSRS pellets which have a considerable amount of ash.

Maoyun He *et al* [98] reported that in the catalytic steam gasification of waste polyethylene, at 750^{o}C, the lower heating value of the gas was 12.15 MJ/m^3, the carbon conversion efficiency was 69% and the cold gas efficiency was 41%. Although the cold gas and carbon conversion efficiencies were in many cases similar to those presented in this work, the heating value of the gas was much higher. This occurred due to the increased amount of H_2 and CH_4 in the gas composition which is a direct result of the steam addition in the gasification process. A similar study by Maschio *et al* [162], reported values of 15.8 MJ/m^3 produced from the steam gasification of a mixture of biomass at 750^{o}C.

A study by Boateng *et al* [163] reports the steam gasification of rice hulls, a fuel with high ash content (21%). The authors reported that gasification at 750^{o}C resulted in a gas higher heating value of 10 MJ/m^3, low gas yield of 0.63m^3/kg and lower than expected carbon conversion efficiency of 43% that was attributed to the higher production of tar and thus a large amount of carbon was retained in the tar.

In a different study [164], during the pyrolysis process of various biomass fuels the highest char yields were produced were of the grape and the tobacco, while the sunflower had the lowest char production. On the other hand, the pyrolysis of sunflower led to higher gas yields during pyrolysis. This is perhaps due to the differences of fixed carbon and volatile content of the fuel. Grape and tobacco have a high fixed carbon content and low volatile content while the vice versa is true for the sunflower. Another difference between the fuels is the different amount of ash. The amount of ash of the sunflower is around 10% while the amount of ash of the grape and tobacco yield is 6% [164].

Umeki *et al* [165] studied the gasification performance of an updraft gasifer using steam. The authors found out that the particle size (10-30 mm) did not have any effect upon the performance which is contradictory with the results of the current project. Furthermore the steam gasification provided higher yields of H_2 and CO_2 and lower amounts of CO and CH_4.

Ash behaviour

One of the most important factors in the biomass gasification and the comparison for different fuels is the behaviour of ash. A report by "Doosan Babcock Energy" [166], sums up three different combinations of mineral species at high temperatures:

1. a low Si, low K and high Ca ash has high fusion temperature
2. a high Si, high K and low Ca ash has low fusion temperature
3. a high Ca and high P ash has low fusion temperature

The Miscanthus pellets partially belong to the first case which despite having a high amount of Si, the melting temperature is higher in comparison to the oilseed rape straw (OSRS) and dried distillers grains with solubles (DDGS) pellets. The two latter types of fuels do not belong in any of the combinations, although sintering was observed during the gasification and this means that the ash behaviour is very complex system and multiple combinations of mineral species could be the cause for the different behaviour of the gasification process which is discussed in this sub-section.

It is important to point out that the ash could act either as a catalyst or could also lead to agglomeration and sintering. The catalytic behaviour of ash has been discussed extensively. There is a positive influence of alkaline catalysts such as NaCl, KCl and LiCl on the yield and gas production [80]. CaO is a catalyst for the water gas shift reaction. Despite the fact that CaO can absorb CO_2, it was found that a bed with an increased amount of CaO could increase the amount of H_2 and CO_2, and decrease the amount of CO due to the catalytic effect of CaO upon the water gas shift reaction that takes CO and transforms it into H_2 and CO_2 [81]. Ikenaga *et al* [167] performed various test on various HCl-treated and untreated biomass to investigate the ash behaviour on the biomass gasification. The authors concluded that the rate of gasification was highly affected by the inherent mineral matter of biomass. Potassium was causing a rapid rise in the gasification rate due to its placement upon the active carbon sites. On the other hand, in fuels that contain a significant amount of both K and Si, there is a danger of deactivation of potassium by the silica by forming potassium silicates which leads to reduced gasification rates. Furthermore the potassium silicate has a low melting temperature that may melt and form a highly viscous liquid that could de-fluidise the spout bed sticking and fusing the sand particles together [168, 169]. In the case of fuels that contain K and Ca inherently in large numbers, the gasification process is catalysed, something that is valid for the E-On Miscanthus pellets as well. The E-On Miscanthus pellets contain large amounts of Ca (26%), high amounts of Si (31.5%) and adequate amounts of K (9%). It is possible that the Si have deactivated the K but the Ca remained as a catalyst for the gasification process, thus increasing the gasification performance. That can be confirmed also by Kannan *et al* [170] who reported that the Si deactivate K by forming catalytically inactive potassium silicates but on the other hand Si does not react with Ca due to the larger basicity of K and lower mobility of Ca species. In addition, the authors [167] point out the fact that only the removal of the alkali and alkaline earth metals was enough for the decline of the gasification performance even though Si and Al were still present, which means that Si and Al on their own are not taking part on the catalysis of gasification. The latter observation can be confirmed in the case of the OSRS pellets which the gasification performance was lower than that of the Miscanthus pellets despite having high amount of Si, Al and adequate amounts of K and Fe. It is important to indicate the catalytic effect of CaO. This is enhanced by the dispersion of CaO on the surface of the char and the strong interaction between metal and carbon [167, 171]. The catalytic effect of CaO decreases with conversion since the increased residence time cause the CaO to sinter. The latter observation was reported by various authors in the literature [167, 172] and can be confirmed by the experiments of the current project especially in the case of Miscanthus pellets which despite the increased gasification efficiency, after an extended amount of time, agglomerates were formed.

The relatively low potassium level of OSRS pellets leads to alternative explanations away from the mainstream "potassium silicate phenomenon", which leads to melting of the ash and thus de-fluidization. It's an accumulation of various phenomena that led to the de-fluidisation of the spout bed at 850^oC. One of the phenomena could be the fact that the OSRS pellets have the highest quantities of Cl among all other pellets, and Cl facilitates the vaporization of the alkalis forming in many cases potassium chloride which is the most stable gas-phase alkali containing species. Thus, it is common that it is the amount of Cl that dictates the vaporized alkalis and not the amount of alkalis [86, 77]. Jordan *et al* [173], conducting experiments using cane bagasse, discovered that during the gasification about 1/3 of K is capture by aluminosilicate structures to be transformed in more stable forms. Half of K is lost in the syngas and 20% stays in a water soluble form without being released to the syngas. On the other hand, 99% of Na stays in the ash while only 35% of Ca and 40% of the Mg stays in the ash. Furthermore Si, occurs by 60% as amorphous Si while the rest appears as crystalline silicates in the aluminosilicates. During gasification the 85% of Si remains as a residue and the rest (15%) is released to the syngas. The lack of large quantities and on the other hand the large quantities of Al and Si in the OSRS pellets possible played a role in the de-fluidization of the spout bed by forming agglomerates. The large volume of agglomerates is consisted of amorphous silica oxide but there are also small amounts of alkali aluminosilicates and several other eutectic formations [173]. Therefore, the melts that were described could have a high potential of facilitating the spout bed de-fluidisation. Thus it is possible to agree in our case due to the large quantities of Si and Al in the OSRS pellets ash.

An interesting phenomenon in comparison of the ash of the large pellets and the small pellets especially in the spout bed case can be seen in Table 6.15. In the case of the small diameters OSRS pellets we can observe high % of Si (25.2%), moderate K (13.5%), low Fe (0.82%) and low Al (0.63%). In the case of the large diameter OSRS pellets we can observe lower Si (21%), lower K (3.7%), higher Fe (3.7%) and higher Al (7.5%). Similar results can be seen in the case of downdraft gasification. An explanation could be the differences in the mobility behaviour. It is possible that mobility depends, among many others, on the potential of a chemical to become volatile, and as already discussed, that the devolatilisation or pyrolysis process of the large pellets was hindered by numerous reasons such as the decreased porosity and increased density of the large pellet, it could also decrease the mobility of the silicates and the alkalis and thus give rise to the rest of the species.

Table 6.15: SEM-EDS analysis of the ash after the gasification process (SD)

Fuel type	O	Mg	Si	P	K	Ca	Fe	Al	Na
OSRS small (spout bed)	51 (±0.44)	1.4 (±0.24)	25.2 (±0.92)	0.64 (±0.08)	13.5 (±0.9)	5.3 (±0.58)	0.82 (±0.23)	0.63 (±0.49)	0
OSRS large (spout bed)	51.2 (±0.31)	1.9 (±0.09)	21 (±0.8)	0	3.7 (±0.7)	6.3 (±1)	3.7 (±0.3)	7.5 (±0.4)	2.2 (±0.2)
Miscanthus (spout bed)	44.6 (±1.4)	1.72 (±0.28)	10.5 (±2)	3.4 (±0.5)	4.4 (±0.4)	23.6 (±4.9)	6 (±1.7)	2.2 (±0.7)	0.56 (±0.2)
OSRS small (downdraft)	51 (±3.6)	1.4 (±0.26)	15.4 (±5.7)	2.2 (±1.2)	15.9 (±1.8)	4.9 (±0.9)	2.6 (±1.3)	0	0
OSRS large (downdraft)	50 (±1.9)	1.7 (±0.4)	15.3 (±5.4)	0.6 (±0.5)	4.9 (±1.8)	8.8 (±3.7)	5.2 (±0.53)	6.2 (±2.3)	1.73 (±0.23)
Miscanthus (downdraft)	49.2 (±2)	2.43 (±0.8)	4.24 (±1.7)	4.7 (±1.4)	7.3 (±1.6)	24.7 (±3.3)	2.3 (±0.29)	1.7 (±0.61)	0.68 (±0.64)
DDGS (downdraft)	50.8 (±2.3)	3.07 (±0.41)	1.3 (±0.4)	13.1 (±2.9)	18.5 (±2.5)	5.1 (±0.82)	2 (±1.96)	0.96 (±0.9)	2.2 (±0.56)

The DDGS pellets have a characteristic ash of high K, very high P, moderate-high Mg and very low Si and Ca. Similar characteristics for fuels such as rye and wheat were reported by Lindstrom *et al* [174]. The authors reported a very high slagging tendency of rye and wheat due to the high Mg, P and K in the fuels. It is possible that a crystalline phase magnesium potassium phosphate and a potassium-rich phosphate melt to be responsible for the melting of the ash even at temperatures as low as 650-680^{o}C. This could be an explanation for the behaviour of DDGS pellets during the downdraft gasification. Furthermore, as it is also mentioned in the literature review, Beck *et al* [88] showed that the presence of Ca reduces the gaseous P compounds and it is possible that the absence of Ca in the DDGS pellets caused the occupation of active sites by the gaseous P, hindering the heat transfer by radiation, which could also lead to an decline in the gasification performance. Furthermore, Steenari *et al* [89] reported that potassium salts in combination with phosphates and high K/Ca ratio, the exact case of DDGS pellets, could lead to low melting temperatures and sintering. As it is mentioned in other studies [174, 89], the problem could be solved with the addition of lime at about 2%wt or calcium carbonate that could completely eliminate the slagging and sintering formation. The addition of lime would lead to the formation of calcium potassium phosphates which have high melting temperature. Grimm *et al* [175] and Onderwater *et al* [176] both reported the stability of phosphate compounds in the ash. In combustion experiments in a fluid bed by Grimm, using fuels with high K and Ca content or fuels with high Si and K content, and also fuels with increased phosphorous (such as DDGS), the addition of phosphorous led to the formation of silicate/phosphate coating layers and led to formation of agglomerates. Despite the initial reaction of the liquid K with the bed material to form a potassium silicate melt and the diffusion of Ca into that melt, the addition of P converted the alkali oxides and the alkaline earth metal oxides into phosphates.

7 Thesis Summary

The main aim of the thesis was to investigate the phenomena that appear during the pelleting process; how these phenomena affect the quality of the pellets; the relationship between the quality of the pellets and the gasification process and finally how the initial pelleting phenomena affect the gasification process. All these were done to connect the pelleting with the gasification process, to immediately foresee the gasification performance by only knowing the initial pelleting parameters.

The main focus of the project was the study of the effect of the initial pelleting parameters, feedstock moisture content, feedstock particle size and die diameter, on the performance of the gasification process. Extreme values (very high or very low) of the pelleting parameters were chosen so that the differences in the gasification performance would be apparent. The main results drew are presented in this chapter.

The first set of results is concerning the amount of amperes (A) and the temperature (^oC) of the pellet rig when the different types of pellets were manufactured. It was found that the differences between type 1 and 2 occur due to the differences in the feedstock particle size. The pellet mill uses additional amount of amps to reduce the size of the large chop and thus its temperature slightly increases. A similar phenomenon was observed in the comparison of pellet types 3 and 4. The differences between pellet type 5 and 6 and also between 7 and 8 were not attributed to the differences in the feedstock particle size but to the addition of lubricants such as oil due to the problems that were occurring during the pelleting process. In addition, the pellets that were manufactured from the dry feed (type 1, 2, 5 and 6) required higher amounts of amps and the die temperature was higher in comparison to the amps and temperature of the pellets that were manufactured from the wet feed (type 3, 4, 7 and 8). This was attributed to the lubricant characteristics of moisture during the pelleting process.

The second set of results is concerning the relationship between the pelleting parameters (feedstock moisture and particle size, die diameter) and the pelleting process (amps, temperature). It was found that the increased feedstock moisture content decreases the amount of amps required by the pellet mill to manufacture the pellets, and thus the die temperature also decreases. Feedstock particle size also has an effect but this effect was observed only in the case of the 5 mm pellets. The larger the feedstock particle size is the higher amount of amps required by the pellet mill, due to the fact that large chop is reduced in size even further inside the die which also increases the die temperature. The phenomenon was not observed in the case of the large 18 mm die. The die diameter also influences the pelleting process. The utilization of the die with the larger diameter (18 mm) required a higher amount of amps and thus the die temperature increased in comparison to what was required by the pellet mill during the utilization of the die with the small diameter (5 mm). The longer die holes of the large die were responsible for higher time periods that the material was inside the holes and thus the material was subjected under higher pressures due to the increased friction factor. From this, it can be seen that the lowest amount of amps was dissipated manufacturing pellets using the small die and the wet and well chopped feed.

The third set of results concerns the correlation of the pelleting process (amps, die temperature) with the pellet quality (pellet density, bulk density, and pellet durability). The correlation of the pelleting process and the pellet density showed that the observed high amount of amps doesn’t always mean pellets of higher density. In our case the wet-feed pellets required smaller amount of amps, due to the lubricant characteristics of moisture, but at the same time their density was higher than the dry-feed pellets. The correlation of the pelleting process and the bulk density showed that the observed high amps meant pellets of higher bulk density while the correlation of the pelleting process and the pellet durability showed that the observed high amps meant that we will have as a result a pellet generally with higher durability.

The fourth set of results concerns the effect of the initial pelleting parameters (feedstock moisture content, feedstock particle size, die diameter) on the pellet quality (pellet density, bulk density and pellet durability). This set of results combines the initial data with the pellet quality and helps to predict the quality of the pellets yielded by choosing certain initial parameters. It was found that the higher feedstock moisture content resulted in a higher pellet density due to the binding characteristics of moisture. It was also found that the higher feedstock moisture content resulted in a decrease of the bulk density as well as a decrease of the pellet durability. The feedstock particle size affected the pellet quality only slightly. Increasing the feedstock particle size resulted in the most of the cases a slight decrease in pellet density, a decrease in the bulk density (only in the case of the large pellets) but no effect was observed on the pellet durability. The die diameter, on the other hand, highly affected the pellet quality. Increasing the die diameter resulted in all the cases in an increase of the pellet density, bulk density and durability.

Overall, for the pelleting process it can be concluded that the highest pellet density of the 5 mm pellets was test 3 (high moisture, small particle size) and of the 18 mm pellets was test 7 which has the same attributes as test 3. The highest bulk density for the 5 mm pellets was observed in test 1 and 2, which means bulk density was not affected by the feedstock particle size while the highest bulk density in the case of the 18 mm pellets was observed in test 5 and 7 meaning that in this case the feedstock particle size slightly affected the bulk density. The highest durability in the case of the 5 mm pellets was observed in tests 1 and 2 while the highest durability in the case of the 18 mm pellets was observed in tests 5 and 6 but with very small differences with the tests 7 and 8.

The pellet quality parameters subsequently affect the gasification process. The 5 mm pellets were successfully gasified in the downdraft gasification rig although for various reasons the efficiency was low. On the other hand, gasification was not achieved in the case of the 18 mm pellets. Gasification in the spout bed was slightly easier to achieve for both sizes due to the higher flexibility of the rig in comparison to the downdraft rig. The gasification performance was firstly correlated with the pellet quality parameters and then with the pelleting manufacturing parameters which is the main goal.

Concerning the effect of pellet density upon the downdraft gasification performance it was found that pellets manufactured from a feed of similar moisture content, even with slightly different pellet density, are more likely to have similar gasification performance. On the contrary, pellets that were manufactured using feed with different moisture contents have an increased probability that their performance would be different and most probably their pellet densities would be different as well, with the pellets manufactured from the wet feed showing higher densities and lower gasification performance. Concerning the effect of bulk density upon the downdraft gasification performance, it was found that the pellets manufactured using the wet feed are more likely to have lower bulk density and decreased gasification performance. On the contrary pellets that were manufactured from the dry feed, showed an increased bulk density which was also correlated with an increased gasification performance. Concerning only the 5 mm pellets, the bulk density of the pellets that were manufactured from similar feed (wet or dry) is too close to identify any changes that might occur in the gasification performance using exactly the same pellets but different bulk densities. Concerning the effect of pellet durability upon the downdraft gasification it was found that the pellets that were manufactured by using the wet feed exhibited lower durability and the lower durability is correlated with a decreased gasification performance in the case of 5 mm pellets.

The effect of the initial pelleting parameters upon the downdraft gasification performance was found to be very significant. It was found that the increased feedstock moisture content not only increases the pellet moisture content but due to the effect that has upon all the pelleting parameters it is negatively correlated to the gasification performance. For example, the high feedstock moisture content was related with a lower heating value (LHV) and a lower cold gas efficiency. The reason is not only that the pellets manufactured by the wet feed have also higher moisture content themselves, but also the fact that the durability and bulk density of these pellets is lower. In general, dry feedstock requires more energy to be handled (dryers etc) but it will also provide a better quality gas in comparison to the wet feed. The optimal solution would be somewhere in the middle (feedstock moisture 8-14% wt) so that we can gain the benefits of a material that is dry enough to be gasified and wet enough to be pelletised. The effect of feedstock particle size upon the downdraft gasification process was studied. It was concluded that it did not have any influence on the gasification performance. The extreme values chosen for the die diameter played a significant role in the downdraft gasification performance. The 5 mm were successfully gasified but the 18 mm pellets couldn't be gasified due to the intolerance of the downdraft gasifier to handle large size fuels. The intolerance of the downdraft gasifier is highly linked to the bed porosity, the quality of the pellet surface reactions the heat transfer performance and others which led to melt of the outer layers, channelling, decreased amount of active carbon sites and others.

The spouted fluidised bed gasification had only few differences in comparison to the downdraft gasification. An addition to the series of tests was the type 8 co-gasification with Miscanthus pellets. More specifically, it is evident that the pellet density correlates negatively with the gasification parameters with two exceptions, the specific energy rate and the gasification rate in which no clear trend can be observed. The highest values detected during the co-gasification. From this we concluded that it is not only the pellet density that plays a role in the gasification process but instead is the quality of the surface reactions. On the other hand it was found that with an increase in the bulk density, the gasification parameters also increase, which is similar to the downdraft gasification, but only in the case of the 5 mm pellets. The effect is not clear for the 18 mm pellets while once again the highest values were observed during the co-gasification for nearly all the cases. In the case of the correlation of durability with the gasification parameters it was found positive in the case of 5 mm pellets (except for the cases of specific energy rate and gasification rate) and unclear in the case of the large pellets. In addition the trend in the case of spouted fluidised bed gasification is similar to the one of the downdraft gasification.

The final target was the investigation of the relationship of the spouted fluidised bed gasification process with the initial pelleting parameters. It was found that the lower the feedstock moisture content, the higher the values are. The effect lost its weight in the case of the CO/CO_2 ratio due to the input condition parameters (even though the ER is similar). About the effect of the feedstock particle size, it was found that the differences are only minor which it means that particle size does play a minor role in the spouted fluidised bed gasification, something that could not be observed in the case of downdraft gasification. The major differences between the pairs, are not the immediate effect of the feedstock particle size though. The major differences are caused by the initial condition parameters even though the equivalence ratio is the same, which means that the initial condition parameters have a weight upon the performance of the spouted fluidised bed gasification in contradiction to the downdraft gasification in which the equivalence ratio seemed to had the major weight (among the condition parameters and the ER). Concerning the effect of die diameter upon the spouted fluidised bed gasification parameters it was found that the extreme value of pellet size decreased the performance of the gasifier in nearly all the parameters except for the specific energy rate and gasification rate. It can be concluded that the two latter values are highly affected by the operating parameters. This was not observed in the downdraft gasification and this means that the operating parameters themselves (with same ER) play a higher role in the spouted fluidised bed in comparison to the downdraft gasification process.

In addition to the effect of the pelleting parameters on the gasification process, other types of biomass were tested and presented; mainly Miscanthus and DDGS pellets. The results were describing the effect of the ER upon the gasification process. About the utilization of Miscanthus pellets in the downdraft rig, it was found that the HHV, cold gas efficiency, carbon conversion efficiency, mass conversion factor, specific energy rate and gasification rate have a positive relation with the increasing equivalence ratio. No correlation was found for CO/CO_2 ratio. The utilization of DDGS pellets in the downdraft rig was tested and found that the HHV, the cold gas efficiency and carbon conversion efficiencies have a positive correlation within the escalating ER. The CO/CO_2 ratio and the specific energy rate did not follow similar trends within the same ER range. On the other hand the mass conversion factor and the gasification rate seem to have a positive correlation within the ER range without this correlation being very clear. The gasification of DDGS pellets it general showed lower efficiencies in comparison to the other biomass feeds due to the implications that the ash have caused. Another fuel that was tested in the downdraft rig was the oilseed rape straw. It was found that the gasification of oilseed rape straw resulted in lower values than the gasification of its pellets except in terms of cold gas end carbon conversion efficiencies. That is possibly because of the lower energy and bulk density of the fuel.

Similar tests using Miscanthus pellets were performed in the spouted fluidised bed. It was found that the cold gas efficiency, the carbon conversion efficiency and the mass conversion factor increasing with increasing ER. That is possibly happening due to the decrease of fuel/air ratio, thus there is more air to react with the fuel. The HHV, on the contrary, shows a decreasing pattern with increasing ER. The ratio of CO/CO_2 is increasing and at the ER value of 0.3 it starts decreasing but the correlation in general was unclear. This is possibly happening due to the enhanced effect of Boudouard reaction because of the increased temperature. Furthermore for the specific energy rate and the gasification rate a weak negative correlation was detected.

Very interesting results were reported in the comparison of the different types of biomass fuels in both downdraft and spouted fluidised bed gasification process. In downdraft gasification the comparison of all the tested fuels showed that Miscanthus pellets have the highest values among all fuels tested, followed by the dry (type 1 and 2) OSRS pellets, the wet (type 3 and 4) OSRS pellets and finally the DDGS pellets. The comparison of the 18 mm OSRS pellets was excluded due to their inability of being gasified. In spouted fluidised bed gasification the comparison of the tested fuels showed that Miscanthus pellets had the best gasification performance among the other fuels, followed in the most of the cases by the co-gasification of type 8 OSRS pellets with Miscanthus pellets, the dry small size OSRS pellets, the wet small size OSRS pellets and finally the large size pellets. An interesting observation was the small differences between the small and large OSRS pellets but the large difference of the two latter with the performance of Miscanthus pellets. This could be an indication that, in the case of spouted fluidised bed gasification, the chemical characteristics has a higher weight than the physical characteristics of the pellets.

The differences among the different types of fuels are mainly attributed to the differences in the ash characteristics. Miscanthus pellets contains high amounts of Ca, K and Si (Si deactivated the K) which catalysed the gasification process. OSRS pellets contain high amounts of Si and Al which do not catalyse the gasification process but instead the catalysis of gasification was performed by small amounts of K. An interesting phenomenon was the differences in residual ash that was exhibited by the gasification of the 5 mm and the 18 mm pellets. The phenomenon was attributed to the differences in ash mobility and devolatilization. In the case of spouted fluidised bed the gasification of OSRS caused the bed to de-fluidise at 850^{o}C. This was attributed to the high amount of Al that resulted in the formation of aluminosilicates and the high amount of Cl that facilitated the alkalis, especially K, to vaporize. Furthermore, DDGS's problematic behaviour was attributed to the high amounts of K and P and to the relatively high amounts of Mg which formed magnesium potassium phosphates and potassium-rich phosphates. In addition, the lack of Ca in the DDGS pellets caused the occupation of active sites by the gaseous P, hindering the heat transfer.

In general the thesis pointed out the importance of the pelleting process upon a thermal conversion process in both qualitative and quantitative ways. The thesis reported the manufacturing and utilization of pellets from cradle to grave showing the economy, in terms of energy dissipation, of pellet manufacturing and their gasification performance. The results could be used to form pelleting standards for pellets to be gasified by implementing them to a wider data collection and also to optimize the pelleting and consequently the gasification process.

8 Conclusions

- Eight different types of pellets manufactured from oilseed rape straw were investigated using the combinations formed by three pelleting parameters: the feedstock moisture content, the feedstock particles size and the die diameter;
- Increasing feedstock moisture content resulted in an increased pellet density, decreased bulk density and decreased pellet durability;
- Increasing the feedstock particle size resulted in the most of the cases a slight decrease in pellet density, a decrease in the bulk density (only in the case of the 18 mm pellets but no effect on the 5 mm pellets) and no effect was observed on the pellet durability;
- Increasing the die diameter resulted in all the cases in an increase of the pellet density, bulk density and durability;
- Downdraft gasification:
    1. The high feedstock moisture content was negatively correlated to the gasification performance. Dry feedstock requires more energy to be handled (dryers etc) but it also provides a better quality gas in comparison to the wet feed;
    2. The feedstock particle size did not have any influence on the gasification performance;
    3. The 5 mm pellets were successfully gasified but the 18 mm couldn’t be gasified;
    4. Miscanthus pellets: it was found that all parameters had a positive relation with the increasing equivalence ratio except for CO/CO_2 ratio where no correlation was found. Correlation was not clear for DDGS pellets;
    5. The comparison of the fuels tested showed that Miscanthus had the best performance followed by the dry (type 1 and 2) OSRS pellets, the wet (type 3 and 4) OSRS pellets and finally the DDGS pellets (valid only for the 5 mm pellets);
- Spouted fluidised bed gasification:
    1. The high moisture content was also negatively correlated with the gasification performance;

2. A minor effect of the feedstock particle size on the gasification performance was detected although the major differences were caused by the condition parameters;
3. The larger diameter pellets decreased the gasification performance in all cases except for the Specific Energy Rate and Gasification Rate which were highly affected by the condition parameters;
4. Miscanthus pellets: it was found that increasing ER was correlated with a decreasing HHV and an increasing Cold Gas Efficiency, Carbon Conversion Efficiency and Mass Conversion Factor;
5. The comparison of the fuels tested showed that Miscanthus pellets had the best gasification performance, followed in the most of the cases by the co-gasification of type 8 OSRS pellets with Miscanthus pellets, the dry small size OSRS pellets, the wet small size OSRS pellets and finally the large size pellets;

- The main reason for the different gasification behaviours among the pellets was identified to be the ash.

9 Contribution to knowledge

The project explored the link between two different processes, the pelletisation and gasification process. This contributes to the prediction of the pellet gasification performance before the manufacturing of the pellets. In addition, despite the fact of oilseed rape being a very important crop in British agriculture, the studies on its straw are limited and this project fills some of the gaps. The interconnection of the pelleting process, the pellet quality and the gasification performance is another contribution to the knowledge.

In summary, the works presented in this thesis demonstrate a clear contribution to knowledge as they highlight the importance of pelleting feedstock and parameters, and the effects of these parameters on the gasification processes. Such comprehensive work on biomass feedstocks and their effects on advanced thermal conversion technologies has not been completed before, and as such this thesis presents findings which are of key importance to this topic.

10 Further work

With the completion of every research new questions are born that could lead to new comprehensive studies. The completion of this project raised some questions that could lead to new research topics:

- Further tests could be performed for more complete ranges of pelleting parameters (especially in the range of 8-14% moisture content, 3-6 mm particle size and 5-18 mm die diameter) and not only for the extreme values of the pelleting parameters;
- Further research should be done for the ash yields and species when using different sizes of pellets in the gasification, as was pointed by this project;
- Other pelleting parameters could be also used such as the addition of binders or oil. Different binders could result in different pellet quality and also different ash characteristics and would be very interesting to investigate which could be the most appropriate binder for gasification and in what amounts;
- Alternative types of fuels should be considered, such as other agricultural residues and energy crops. Their differences in the ash content would constitute a research in pellet binders imperative to find the most appropriate for each of the fuels especially if the pellets are to be used in gasification;
- Alternative types of gasification technique could be also used such as the updraft, the fluid bed and the spout-fluid bed gasification in order to investigate optimum pelleting parameters for these techniques as well;
- Similar tests and methods could be performed for other thermal conversion processes, such as combustion and pyrolysis, in order to optimize the pelleting process accordingly. Optimization of the pelleting and the gasification process would help to combine the two processes in single small scale or medium scale units and that would facilitate the de-centralization and redistribution of energy.

References

[1] Keranen, J., Alakangas, E. ***Report on the competition and price situation of woody biomass use in forest industry and energy sector***, EUBIONET3, May 2011.

[2] Junginger, M., Van Dam, J., Alakangas, E., Virkkunen, M., Vesterinen, P. and Veijonen, K. ***Solutions to overcome barriers in bioenergy markets in Europe – D2.2***, EUBIONET 3 February 2010.

[3] Olsson, O., Vinterback J., Dahlberg A., Porso C. ***Price mechanisms for wood fuels***, EUBIONET3, April 2010.

[4] European Environment Agency. ***How much energy can Europe produce without harming the environment?***, EEA report No 7/2006.

[5] Panoutsou C. and Perry M. ***WP2 – Biomass fuel trade in Europe; Country Report: United Kingdom***, Imperial College London, EUBIONET3: October 2009.

[6] European Environmental Agency. ***Estimating the environmentally compatible bioenergy potential from agriculture***, Technical report No12/2007.

[7] Department for Environment, Food and Rural Affairs (DEFRA). ***Agriculture in the United Kingdom 2010***.

[8] Office of gas and electricity markets. ***Typical domestic energy consumption figures***, Factsheet 96, 18.01.11, http://www.ofgem.gov.uk

[9] Department of Energy and Climate Change. ***UK renewable energy roadmap***, July 2011.

[10] Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing directives 2001/77/EC and 2003/30/EC.

[11] Eurostat. ***Europe in figures – Eurostat yearbook 2010: Environment and Energy.***

[12] Eurostat. ***Europe in figures – Eurostat yearbook 2011: Energy.***

[13] Diaz-Chavez, R. A. ***Country report of different criteria for sustainability and certification of biomass and solid, liquid and gaseous biofuels***, Centre for Environmental Policy, February 2010.

[14] Department of energy and climate change. ***Digest of United Kingdom energy statistics 2010***, National Statistics Publication, 2010.

[15] Pellets atlas. ***Pellet market country report UK***, The National Energy Foundation, National Energy Centre, April 2009.

[16] European Biomass Association. ***Annual statistical report on the contribution of biomass to the energy system in the EU27***, AEBIOM: 2011.

[17] Olsson, O., Vinterback, J. and Porso, C. ***Wood fuel price statistics in Europe***, EUBIONET 3, 2010.

[18] HM Government. ***Meeting the energy challenge. A white paper on energy***, dti, May 2007.

[19] Burke James. ***Connections***, Simon and Schuster Paperbacks, 2007.

[20] Spath, P.L., Dayton, D.C. **Preliminary Screening – Technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas**, National Renewable Energy Laboratory, December 2003.

[21] Kirkels, A.F., Verbong, G.P.J. Biomass gasification: Still promising? A 30-year global overview. ***Renewable and sustainable energy reviews***, 15, 2011, p. 471-481.

[22] Commission of the European Communities. Proposal for a Directive of the European Parliament and of the Council on the promotion of the use of energy from renewable sources, Brussels 23.1.2008.

[23] Ricklefs, Robert E., Miller Gary L. ***Ecology***, 4th ed, W.H. Freeman and Company, USA: 2000.

[24] Klass, Donald L. ***Biomass for renewable energy fuels and chemicals***, Academic press, 1998.

[25] Wagland, Stuart Thomas. ***Development and evaluation of a rapid enzymatic hydrolysis test method to assess the biodegradability of organic waste***, Cranfield University, 2008.

[26] Twidell, John and Weir, Tony. ***Renewable energy resources***, 2nd ed. Taylor and Francis, 2006.

[27] Department for Environment, Food and Rural Affairs. ***UK Biomass Strategy***, 2007.

[28] http://www.oregon.gov/ENERGY/RENEW/Biomass/BiomassHome.shtml, 24/07/2009.

[29] Boyle, Godfrey. ***Renewable energy. Power for a sustainable future***, 2nd ed. Oxford University Press and The Open University, 2004.

[30] Blamey, Marjorie., Grey-Wilson, Christopher. ***The Illustrated Flora of Britain and Northern Europe***, Domino books, 1989.

[31] Farm direct, http://www.farm-direct.co.uk/farming/stockcrop/rape/index.html, 13/01/2009.

[32] Carruthers, S.P. Potential developments and market-size limitations for new oilseed-rape opportunities. In: ***Proceedings of the ninth international rapeseed congress. Rapeseed today and tomorrow***, Vol 4, 1995.

[33] Ward, J.T., Basford, W.D., Hawkins, J.H., Holliday, J.M. ***Oilseed rape***, Farming Press Ltd, 1985.

[34] http://www.ukagriculture.com/crops/oil_seed_rape.cfm , 23/08/2010.

[35] http://www.biomassenergycentre.org.uk/portal/page?_pageid=75,17972&_dad=portal&_schema=PORTAL, 23/08/2010.

[36] DEFRA. ***Joint announcement by the agricultural departments of the United Kingdom. Cereals and oilseed rape production estimates: 2009 harvest, UK, final results***, 2010, http://www.defra.gov.uk/evidence/statistics/foodfarm/food/cereals/documents/cps_osr_mincrop_final.pdf

[37] http://www.defra.gov.uk/evidence/statistics/foodfarm/enviro/observatory/indicators/c/c2_data.htm, Defra, 06/08/2010.

[38] Jones, M. B., McCarthy, S., Keane, R., Halbert, C. Miscanthus Productivity Network. In: ***Biomass for energy and industry***, 7th E.C. Conference, 1994.

[39] Lledo, M.D., Renvoize, S.A., Chase, M.W. Miscanthus sinensis and Miscanthus sacchariflorus: a confusing pair of species. In: ***Aspects of applied biology 65, Biomass and energy crops II***, 2001.

[40] Nixon, P.M.I., Bullard, M.J. Is Miscanthus suited to the whole of England and Wales? Preliminary studies. In: ***Aspects of applied biology 65, Biomass and energy crops II***, 2001.

[41] Baxter, X.C., Christodoulou, A., Darvell, L.I., Jones, J.M., Yates, N.E., Shield, I., Barraclough, T. Influence of particle size on the analytical and chemical properties of Miscanthus as an energy crop. In: ***Proceedings of the Bioten conference on biomass, bioenergy and biofuels 2010***, 2011.

[42] Kumar, A., Demirel, Y., Jones, D.D., Milford, A.H. Optimization and economic evaluation of industrial gas production and combined heat and power generation from gasification of corn stover and distillers grains. ***Bioresource technology***, 101, 2010, p. 3696-3701.

[43] Tavasoli, A., Ahangari, M.G., Soni, C., Dalai, A.K. Production of hydrogen and syngas via gasification of the corn and wheat dry distillers grains (DDGS) in a fixed-bed micro reactor. ***Fuel processing technology***, 90, 2009, p. 472-482.

[44] Tiffany, D.G., Morey R.V., De Kam M.J. Economics of biomass gasification/combustion at fuel ethanol plants. ***Applied engineering in agriculture***, 25(3), 2007, p. 391-400.

[45] Demirbas, Ayhan. Combustion characteristics of different biomass fuels. ***Progress in energy and combustion science***, 30, 2004, p. 219-230.

[46] Mani, S., Tabil, L.G., Sokhansanj, S. Effects of compressive force, particle size and moisture content on mechanical properties of biomass pellets from grasses. ***Biomass and bioenergy***, 30, 2006, p. 648-654.

[47] Samson, R. and Duxbury, P. ***Assessment of Pelletized Biofuels***, Resource efficient agricultural production – Canada: April 2000.

[48] Strehler, A., Stutzle, W. Biomass residues. In: ***Biomass regenerable energy***, edited by D.O.Hall, R.P.Overend, 1987, John Wiley and sons.

[49] Chen, Q., Swithenbank, J., Sharifi, V.N. ***Review of biomass and solid recovered fuel (SRF) pelletisation technologies***, EPSRC Supergen bioenergy theme 4 (heat and power), SUWIC, Sheffield University, February 2008.

[50] Sokhansanj, S., Mani, S., Bi, X., Zaini, P., Tabil, L. Binderless pelletisation of biomass. ASAE, ***The society for engineering in agricultural, food and biological systems***, ASAE Annual International Meeting, 17-20 July 2005.

[51] Ryu, Changkook, Finney, K., Sharifi, V.N., Swithenbank, J. Pelletised fuel production from coal tailings and spent mushroom compost – part I, Identification of pelletisation parameters. ***Fuel processing technology***, 89, 2008, p. 269-275.

[52] Tabil, L.G., Sokhansanj, S., Tyler, RT. Performance of different binders during alfalfa pelleting. ***Canadian agricultural engineering***, 39(1), 1997, p. 17-23.

[53] Kaptay, G. Classification and general derivation of interfacial forces, acting on phases, situated in the bulk, or at the interface of other phases. Proceedings of the IV international conference / High temperature capillarity, ***Journal of materials science***, 40, 2005, p. 2125-2131.

[54] Van Dam, J.E.G., Van den Oever, M.J.A., Teunissen, W., Keijsers E.R.P., Peralta A.G. Process for production of high density / high performance binderless boards from whole coconut husk. Part 1: Lignin as intrinsic thermosetting binder resin. ***Industrial crops and products***, 19, 2004, p. 207-216.

[55] White, R.H. Effect of lignin content and extractives on the higher heating value of wood. ***Wood and fiber science***, 19(4), 1987, p. 446-452.

[56] Lehtikangas, P. Quality properties of pelletised sawdust, logging residues and bark. ***Biomass and bioenergy***, 20, 2001, p. 351-360.

[57] Kaliyan, N., Morey, R.V. Factors affecting strength and durability of densified biomass products. ***Biomass and bioenergy***, 33, 2009, p. 337-359.

[58] Briggs, J.L., Maier, D.E., Watkins, B.A., Behnke, K.C. Effect of ingredients and processing parameters on pellet quality. ***Poultry Science***, 78, 1999, p. 1464-1471.

[59] Larsson, S.H., Thyrel, M., Geladi, P., Lestander, T.A. High quality biofuel pellet production from pre-compacted low density raw materials. ***Bioresource technology***, 99, 2008 p. 7176-7182.

[60] Bridgeman, T.G., Darvell, L.I., Jones, J.M., Williams, P.T., Fahmi, R., Bridgewater, A.V., Barraclough, T., Shield, I., Yates, N., Thain, S.C., Donnison, I.S. Influence of particle size on the analytical and chemical properties of two energy crops. ***Fuel***, 86, 2007 p. 60-72.

[61] Sokhansanj, S., Tabil, L., Yang, W. Characteristics of plant tissues to form pellets. ***Powder handling and processing***, 11(2), 1999.

[62] Obernberger, I., Thek, G. Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behaviour. ***Proceedings of the 1st World conference on pellets***, Sept 2002, p. 115-122.

[63] Sokhansanj, S., Mani, S., Bi, X., Zaini, P., Tabil, Lope. Binderless pelletization of biomass. ***ASAE annual international meeting***, 17-20 July 2005.

[64] Mani, S., Sokhansanj, S., Bi, X., Turhollow, A. Economics of producing fuels pellets from biomass. ***Applied engineering in agriculture***, 22(3), 2006, p. 421-426.

[65] Quaak, P., Knoef, H. and Stassenm, H. ***Energy from biomass. A review of combustion and gasification technologies***, World Bank technical paper No. 422 Energy Series, March 1999.

[66] Basu, Prabir. ***Combustion and gasification in fluidized beds***, CRC press, Taylor and Francis Group, 2006.

[67] de Souza-Santos, M.L. ***Solid fuels combustion and gasification. Modeling simulation and equipment operation***, Marcel Dekker Inc, 2004.

[68] Raveendran, K., Ganesh, A., Khilar, K.C. Pyrolysis characteristics of biomass and biomass components. ***Fuel***, 75(8), 1996, p. 987-998.

[69] Reed, T.B., Markson, M. A predictive model for stratified downdraft gasification of biomass. ***Progress in biomass conversion***, 4, 1983, p. 217-254.

[70] Hos, J.J., Groeneveld, M.J. Biomass gasification. In: ***Biomass regenerable energy***, Edited by D O Hall and R P Overend, John Wiley and Sons Ltd, 1987.

[71] Higman, C., Van der Burgt, M. ***Gasification***, Gulf Professional Publishing, Elsevier, 2003.

[72] Jarungthammachote, S., Dutta, A. Equilibrium modelling of gasification: Gibbs free energy minimisation approach and its application to spouted bed and spout-fluid bed gasifiers. ***Energy conversion and management***, 49, 2008, p. 1345-1356.

[73] Di Blasi, Colomba. Combustion and gasification rates of lignocellulosic chars. ***Progress in energy and combustion science***, 35, 2009, p. 121-140.

[74] Basu, Prabir. ***Biomass gasification and pyrolysis***, Academic press Inc, 2010.

[75] Gas production. In: ***Ullmann's Encyclopedia of Industrial Chemistry***, Volume A12.

[76] Faaij, A., van Ree, R., Waldheim, L., Olsson, E., Oudhuis, A., van Wijk, A., Daey-Ouwens, C., Turkenburg, W. Gasification of biomass wastes and residues for electricity production. ***Biomass and bioenergy***, 12(6), 1997, p. 387-407.

[77] Jenkins, B.M., Baxter, L.L., Miles Jr, T.R., Miles, T.R. Combustion properties of biomass. ***Fuel processing technology***, 54, 1998, 17-46.

[78] Erlich, C., Bjornbom, E., Bolado, D., Giner, M., Fransson, T.H. Pyrolysis and gasification of pellets from sugar cane bagasse and wood. ***Fuel***, 85, 2006, p. 1535-1540.

[79] dos Santos, F.J., Goldstein Jr, L. Experimental aspects of biomass fuels in a bubbling fluidized bed combustor. ***Chemical engineering and processing***, 47, 2008, p. 1541-1549.

[80] Encinar, J.M., Gonzalez, J.F., Rodriguez, J.J., Ramiro, M.J. Catalysed and uncatalysed steam gasification of eucalyptus char: influence of variables and kinetic study. ***Fuel***, 80, 2001, p. 2025-2036.

[81] Weerachanchai, P., Horio, M., Tangsathitkulchai, C. Effects of gasifying conditions and bed materials on fluidized bed steam gasification of wood biomass. ***Bioresource technology***, 100, 2009, p. 1419-1427.

[82] Chen, J.S., Gunkel, W.W. Modeling and simulation of co-current moving bed gasification reactors – Part II. A detailed gasifier model. ***Biomass***, 14, 1987, p. 75-98.

[83] Mitsuoka, K., Hayashi, S., Amano, H., Kayahara, K., Sasaoaka, E., Uddin, Md.A. Gasification of woody biomass char with CO_2: The catalytic effect of K and Ca species on char gasification reactivity. ***Fuel processing technology***, 92, 2011, p. 26-31.

[84] Moulijn, J.A., van Diepen, A.E., Kapteijn, F. Catalyst deactivation: is it predictable? What to do? ***Applied Catalysis***, A: General, 212, 2001, p. 3-16.

[85] Miles, T.R., Miles Jr, T.R., Baxter, L.L., Bryers, R.W., Jenkins, B.M. and Oden L.L. Boiler deposits from firing biomass fuels. ***Biomass and bioenergy***, 10(2-3), 1996, p. 125-138.

[86] Baxter, L.L., Miles, T.R., Miles Jr, T.R., Jenkins, B.M., Milne, T., Dayton, D., Bryers, R.W., Oden, L.L. The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences. ***Fuel processing technology***, 54, 1998, p. 47-78.

[87] Monti, A., Di Virgilio, N., Venturi, G. Mineral composition and ash content of six major energy crops. ***Biomass and Bioenergy***, 32, 2008, p. 216-223.

[88] Beck, J., Unterberger, S. The behaviour of phosphorus in the flue gas during the combustion of high-phosphate fuels. ***Fuel***, 85, 2006, p. 1541-1549.

[89] Steenari, B.M., Lundberg, A., Pettersson, H., Wilewska-Bien, M., Andersson, David. Investigation of ash sintering during combustion of agricultural residues and the effect of additives. ***Energy fuels***, 23, 2009, p. 5655-5662.

[90] Rhen, C., Ohman, M., Gref, R., Wasterlund, I. Effect of raw material composition in woody biomass pellets on combustion characteristics. ***Biomass and bioenergy***, 31, 2007, p. 66-72.

[91] Bridgwater, A.V. The technical and economic feasibility of biomass gasification for power generation. ***Fuel***, 74(5), 1995, p. 631-653,

[92] Epstein, N. and Grace, J.R. ***Spouted and spout-fluid beds. Fundamentals and applications***, Cambridge University Press, 2011.

[93] Cui, H., Grace, J.R. Spouting of biomass particles: A review. ***Bioresource technology***, 99, 2008, p. 4008-4020.

[94] Alazar, M., San Jose, M.J., Aguayo, A.T., Arandes, J.M., Bilbao, J. Design factors of conical spouted beds and jet spouted beds. ***Industrial and engineering chemistry research***, 32, 1993, p. 1245-1250.

[95] Bi, H.T., Macchi, A., Chaouki, J., Legros, R. Minimum spouting velocity of conical spouted beds. ***The Canadian journal of chemical engineering***, 75(2), 1997, p. 460-465.

[96] Blasiak, W., Szewczyk, D., Lucas, C. Gasification of biomass wastes with high temperature air and steam. ***21st International Conference on incineration and thermal treatment technologies***, New Orleans, USA, May 2002.

[97] Radmanesh, R., Chaouki, J., Guy, C. Biomass gasification in a bubbling fluidized bed reactor: experiments and modelling. ***Environmental engineering and science***, 52(12), 2006 p. 4258-4272.

[98] Maoyun He, Bo Xiao, Zhiquan Hu, Shiming Liu, Xianjun Guo, Siyi Luo. Syngas production from catalytic gasification of waste polyethylene: Influence of temperature on gas yield and composition. ***International journal of hydrogen energy***, 34, 2009, p. 1342-1348.

[99] Rao, M.S., Singh, S.P., Sodha, M.S., Dubey, A.K., Shyam, M. Stoichiometric, mass, energy and exergy balance analysis of countercurrent fixed-bed gasification of post consumer residues. ***Biomass and bioenergy***, 27, 2004, p. 155-171.

[100] Lv, P.M., Xiong, Z.H., Chang, J., Wu, C.Z., Chen, Y., Zhu, J.X. An experimental study on biomass air-steam gasification in a fluidized bed. ***Bioresource Technology***, 95, 2004, 95-101.

[101] Geldart, D. Types of gas fluidization. ***Powder Technology***, 7, 1973, p. 285-292.

[102] Heffner, L.E., Pfost, H.B. Gelatinization during pelleting. ***Feedstuff***, 45, 1973, p. 33.

[103] Pfost, H.B. The effect of lignin binders, die thickness and temperature on the pelleting process. ***Feedstuffs***, 36(20), 1964, p. 54.

[104] Gilbert, P., Ryu, C., Sharifi, V., Swithenbank, J. Effect of process parameters on pelletisation of herbaceous crops. ***Fuel***, 88, 2009, p. 1491-1497.

[105] Tabil Jr, L., Sokhansanj, S. Process conditions affecting the physical quality of Alfalfa pellets. ***Applied energy in agriculture***, 12(3), 1996, p. 345-350.

[106] Gustafson, A.S., Kjelgaard, W.L. Hay pellet geometry and stability. ***Agricultural engineering***, 44(8), 1963, p. 442-445.

[107] Smith I.E., Probert S.D., Stokes R.E., Hansford R.J. The briquetting of wheat straw. ***Journal of agricultural engineering research***, 22, 1977, p. 105-111.

[108] Kaliyan, N., Morey, R.V. Densification of corn stover. ASAE paper no. 056134, St. Joseph, MI: ***ASABE***, 2005.

[109] O'Dogherty, M.J., Wheeler, J.A. Compression of straw to high densities in closed cylindrical dies. ***Journal of agricultural engineering research***, 29, 1984, p. 61-72.

[110] Obernberger, I. and Thek G. ***The pellet handbook. The production and thermal utilization of biomass pellets***. First publication, Earthscan, 2010.

[111] Dobie, J.B. Engineering appraisal of hay pelleting. ***Agricultural engineering***, 40(2), 1959, p. 76-72.

[112] Lam, P.S., Sokhansanj, S., Bi, X., Lim, C.J., Naimi, J., Hoque, M., Mani, S., Womac, A.R., Ye, X.P., Narayan, S. Bulk density of wet and dry wheat straw and switchgrass particles. ***Applied engineering in agriculture***, 24(3), 2008, p. 351-358.

[113] Hill, B., Pulkinen, D.A. A study of factors affecting pellet durability and pelleting efficiency in the production of the dehydrated Alfalfa pellets. ***Saskatchewan Dehydrators Association***, 1998, p. 25.

[114] Singh, D., Kashyap, M.M. Mechanical and combustion characteristics of paddy husk briquettes. ***Agricultural waste***, 13, 1985, p. 189-196.

[115] Pietsch, Wolfgang. ***Agglomeration processes - Phenomena, technologies, equipment***, Wiley-VCH, 2002.

[116] Zainal, Z.A., Ali, R., Lean, C.H., Seetharamu, K.N. Prediction of performance of a downdraft gasifier using equilibrium modeling for different biomass materials. ***Energy conversion and management***, 42, 2001, p. 1499-1515.

[117] Sharma, A.Kr. Equilibrium modeling of global reduction reactions for a downdraft (biomass) gasifier. ***Energy conversion and management***, 49, 2008, p. 832-842.

[118] Jarungthammachote, S., Dutta, A. Thermodynamic equilibrium model and second law analysis of a downdraft waste gasifier. ***Energy***, 32, 2007, p. 1660-1669.

[119] Rajvanshi, A.K. Biomass gasification. In: ***Alternative energy in agriculture***, Vol. II, Ed. D. Yogi Goswami, CRC Press, 1986, chapter 4, p. 83-102.

[120] Walawender, W.P., Chee C.S., Fan, L.T. Operating parameters influencing downdraft gasifier performance. In: ***Energy from biomass and wastes***, Editor: DL Klass, 1988, 411-445.

[121] Van Heek, K.H., Muhlen, H.J. Chemical kinetics of carbon and char gasification. In: ***Fundamental issues in control of carbon gasification reactivity***, Kluwer academic publisher, 1991, 1-34.

[122] Di Blasi, Colomba. Kinetic modelling of biomass gasification and combustion. ***Thermal Net***, Intelligent energy.

[123] Cetin, E., Moghtaderi, B., Gupta, R., Wall, T. F. Influence of pyrolysis conditions on the structure and gasification reactivity of biomass chars. ***Fuel***, 83, 2004, p. 2139-2150.

[124] Tinaut, F.V., Melgar, A., Perez, J.F., Horrillo, A. Effect of biomass particle size and air superficial velocity on the gasification process in a downdraft fixed bed gasifier. An experimental and modelling study. ***Fuel processing technology***, 89, 2008, p. 1076-1089.

[125] Botts, J.W. Mass transfer coefficients developed from the air gasification of wood pellets. ***American society of mechanical engineers***, Fuels and combustion technologies division, FACT - 22, 1998, p. 321-328.

[126] Erlich, C., Fransson, T.H. Downdraft gasification of pellets made of wood, palm-oil residues respective bagasse: Experimental study. ***Applied Energy***, 88, 2011, p. 899-908.

[127] Feng Yan, Leguan Zhang, Zhiquan Hu, Gong Cheng, Chengcheng Jiang, Yanli Zhang, Tao Xu, Piwen He, Siyi Luo, Bo Xiao. Hydrogen-rich gas production by steam gasification of char derived from cyanobacterial blooms (CDGB) in a fixed-bed reactor: Influence of particle size and residence time on gas yield and syngas composition. ***International journal of hydrogen energy***, 35, 2010, p. 10212-10217.

[128] Standish, N., Tanjung, A.F.A. Gasification of single wood charcoal particles in CO_2. ***Fuel***, 67(5), 1988, 666-672.

[129] Erlich, C., Ohman, M., Bjornbom, E., Fransson, T.H. Thermochemical characteristics of sugar cane bagasse pellets. ***Fuel***, 84, 2005, p. 569-575.

[130] Reed, T.B., Levie, B. A simplified model of the stratified downdraft gasifier. In: ***International bio-energy directory and handbook***, edited by Paul F. Bente, Jr, 1984, p. 379-389.

[131] Radovic, L.R., Walker Jr, P.L., Jenkins, R.G. Importance of carbon active sites in the gasification of coal chars. ***Fuel***, 62(7), 1983, p. 849-856.

[132] Ollero, P., Serrera, A., Arjona, R., Alcantarilla, S. Diffusional effects in TGA gasification experiments for kinetic determination. ***Fuel***, 81, 2002, 1989-2000.

[133] Mani, T., Mahinpey, N., Murugan, P. Reaction kinetics and mass transfer studies of biomass char gasification with CO_2. ***Chemical engineering science***, 66, 2011, p. 36-41.

[134] Jalan, R.K., Srivastava, V.K. Studies on pyrolysis of a single biomass cylindrical pellet – kinetic and heat transfer effects. ***Energy conversion and management***, 40, 1999 p. 467-494.

[135] Mathur, K.B., Gishler, P.E. A study of the application of the spouted bed technique to wheat drying. ***Journal of applied chemistry***, 5(11), 1955, 624-636.

[136] Hoque, M.M., Bhattacharya, S.C. Fuel characteristics of gasified coconut shell in a fluidized and a spouted bed reactor. ***Energy***, 26, 2001, p. 101-110.

[137] Pellegrini, L.F., de Oliveira Jr, S. Exergy analysis of sugarcane bagasse gasification. ***Energy***, 32, 2007, p. 314-327.

[138] Sanz, A., Corella, J. Modeling circulating fluidized bed biomass gasifiers. Results from a pseudo-rigorous 1-dimensional model for stationary state. ***Fuel processing technology***, 87, 2006, p. 247-258.

[139] Hernandez, J.J., Aranda-Almansa, G., Bula, A. Gasification of biomass wastes in an entrained flow gasifier: Effect of the particle size and the residence time. ***Fuel processing technology***, 91, 2010, p. 681-692.

[140] Zanzi, R., Sjostrom, K., Bjornbom, E. Rapid high-temperature pyrolysis of biomass in a free-fall reactor. ***Fuel***, 75(5), 1996, p. 545-550.

[141] Koufopanos, C.A., Papayannakos, N. Modelling of the pyrolysis of biomass particles. Studies on kinetics, thermal and heat transfer effects. ***Canadian journal of chemical engineering***, 69(4), 1991, 907-915.

[142] Rapaga, S., Latif, A. Steam gasification of almond shells in a fluidised bed reactor: The influence of temperature and particle size on product yield and distribution. ***Biomass and bioenergy***, 12(4), 1997, p. 281-288.

[143] Semino, D., Tognotti, L. Modelling and sensitivity analysis of pyrolysis of biomass particles in a fluidised bed. ***Computers and chemical engineering***, 22, 1998, p. S699-S702.

[144] Beaumont, O., Schwob, Y. Influence of physical and chemical parameters on wood pyrolysis. ***Industrial and engineering chemistry process design and development***, 23, 1984, p. 637-641.

[145] McKendry, P. Energy production from biomass part 3: gasification technologies. ***Bioresource technology***, 83, 2002, p. 55-63.

[146] Wang, Y., Kinoshita, C.M. Experimental analysis with biomass gasification with steam and oxygen. ***Solar energy***, 49(3), 1992, p. 153-158.

[147] Chen Hanping, Li Bin, Yang Haiping, Tang Guolai, Zhang Shihong. Experimental investigation of biomass gasification in a fluidized bed reactor. ***Energy and fuels***, 22, 2008, p. 3493-3498.

[148] Turn, S., Kinoshita, C., Zhang, Z., Ishimura, D., Zhou, J. An experimental investigation of hydrogen production from biomass gasification. ***International journal hydrogen energy***, 23(8), 1998, p. 641-648.

[149] Narvaez, I., Orio, A., Aznar, M.P., Corella, J. Biomass gasification with air in an atmospheric bubbling fluidized bed. Effect of six operational variables on the quality of the produced raw gas. ***Industrial and engineering chemistry research***, 35, 1996, p. 2110-2120.

[150] Gil, J., Corella, J., Aznar, M.P., Caballero, M.A. Biomass gasification in atmospheric and bubbling fluidized bed: Effect of the type of gasifying agent on the product distribution. ***Biomass and bioenergy***, 17, 1999, p. 389-403.

[151] Mansaray, K.G., Ghaly, A.E., Al-Taweel, A.M., Hamdullahpur, F., Ugursal, V.I. Air gasification of rice husk in a dual distributor type fluidized bed gasifier. ***Biomass and bioenergy***, 17, 1999, p. 315-332.

[152] Nikoo, M.B., Mahinpey, N. Simulation of biomass gasification in fluidized bed reactor using ASPEN PLUS. ***Biomass and bioenergy***, 32, 2008, p. 1245-1254.

[153] Manya, J.J., Sanchez, J.L., Abrego, J., Gonzalo, A., Arauzo, J. Influence of gas residence time and air ratio on the air gasification of dried sewage sludge in a bubbling fluidised bed. ***Fuel***, 85, 2006, p. 2027-2033.

[154] Garcia-Bacaicoa, P., Bilbao, R., Arauzo, J., Salvador, M. L. Scale-up of downdraft moving bed gasifiers (25-300 kg/h) – Design, experimental aspects and results. ***Bioresource technology***, 48, 1994, p. 229-235.

[155] Ergudenler, A., Ghaly, A.E. Quality of gas produced from wheat straw in a dual-distributor type fluidized bed gasifier. ***Biomass and bioenergy***, 3(6), 1992, p. 419-430.

[156] Phyllis database, http://www.ecn.nl/phyllis/dataTable.asp, 21/02/12.

[157] Janicek, B. N., Kononoff, P. J., Gehman, A. M., Doane, P. H. The Effect of Feeding Dried Distillers Grains Plus Solubles on Milk Production and Excretion of Urinary Purine Derivatives. ***Faculty Papers and Publications in Animal Science***, Paper 599, University of Nebraska – Lincoln, 2008.

[158] Butterman, H.C., Castaldi M.J. Influence of CO_2 injection on biomass gasification. ***Industrial and engineering chemistry research***, 46, 2007, p. 8875-8886.

[159] Dangzhen Lv, Minghou Xu, Xiaowei Liu, Zhonghua Zhan, Zhiyuan Li, Hong Yao. Effect of cellulose, lignin, alkali and alkaline earth metallic species on biomass pyrolysis and gasification. ***Fuel processing technology***, 91, 2010, p. 903-909.

[160] Karim Ghani, W.A.W.A., Moghadam, R.A., Mohd Salleh, M.A., Alias, A.B. Air gasification of agricultural waste in a fluidized bed gasifier: Hydrogen production performance. ***Energies***, 2, 2009, p. 258-268.

[161] Haykiri-Acma, H., Yaman, S., Kucukbayrak, S. Gasification of biomass chars in steam-nitrogen mixture. ***Energy conversion and management***, 47, 2006, p. 1004-1013.

[162] Maschio, G., Lucchesi, A., Stoppato, G. Production of syngas from biomass. ***Bioresource technology***, 48, 1994, p. 119-126.

[163] Boateng, A.A., Walawender, W.P., Fan, L.T., Chee, C.S. Fluidized-bed steam gasification of rice hull. ***Bioresource technology***, 40, 1992, p. 235-239.

[164] Encinar, J.M., Beltran, F.J., Gonzalez, J.F., Moreno, M.J. Pyrolysis of maize, sunflower, grape and tobacco residues. ***Journal of chemical technology and biotechnology***, 70, 1997, p. 400-410.

[165] Umeki, K., Namioka, T., Yoshikawa, K. Analysis of an updraft biomass gasifier with high temperature steam using a numerical model. ***Applied energy***, 90, 2012, p. 38-45.

[166] Livingstone, W.R. Biomass ash characteristics and behaviour in combustion, gasification and pyrolysis systems. ***Doosan Babcock Energy***, Report No: 34/07/005, issue 1

[167] Ikenaga, N., Nakajima, H., Oda, H., Suzuki, T. CO_2 gasification behaviour of various biomass chars. ***Science and technology reports of Kansai University***, No. 51, 2009

[168] Zevenhoven-Onderwater, M., Backman, R., Skrifvars, B.J., Hupa, M., Liliendahl, T., Rosen, C., Sjostrom, K., Engvall, K., Hallgren, A. The ash chemistry in fluidised bed gasification of biomass fuels. Part II: Ash behaviour prediction versus bench scale agglomeration tests. ***Fuel***, 80, 2001, p. 1503-1512.

[169] Fryda, L.E., Panopoulos, K.D., Kakaras, E. Agglomeration in fluidised bed gasification of biomass. ***Powder technology***, 181, 2008, p. 307-320.

[170] Kannan, M.P., Richards, G.N. Gasification of biomass chars in carbon dioxide: dependence of gasification rate on the indigenous metal content. ***Fuel***, 69, 1990, p. 747-753.

[171] Suzuki, T., Ohme, H., Watanabe, Y. Mechanisms of alkaline earth metals catalyzed CO2 gasification of carbon,. ***Energy and fuels***, 8, 1994, p. 649-658.

[172] Radivic, L.R., Walker Jr, P.L., Jenkins, R.G. Effect of lignite pyrolysis conditions on calcium oxide dispersion and subsequent char reactivity. ***International symposium: Fundamentals of catalytic coal and carbon gasification***, Amsterdam, 1982.

[173] Jordan, C.A., Akay, G. Speciation and distribution of alkali, alkali earth metals and major ash forming elements during gasification of fuel cane bagasse. ***Fuel***, 91, 2012, p. 253-263

[174] Lindstrom, E., Sandstrom, M., Bostrom, D., Ohman, M. Slagging characteristics during combustion of cereal grains rich in phosphorus. ***Energy and fuels***, 21, 2007, p. 710-717.

[175] Grimm, A., Skoglund, N., Bostrom, D., Ohman, M. Bed agglomeration characteristics in fluidized quartz bed combustion of phosphorus-rich biomass fuels. ***Energy fuels***, 25, 2011, 937-947.

[176] Zevenhoven-Onderwater, M., Backman, R., Skrifvars, B.J., Hupa, M. The ash chemistry in fluidised bed gasification of biomass fuels. Part I: predicting the chemistry of melting ashes and ash-bed material interaction. ***Fuel***, 80, 2001, p. 1489-1502.

Appendix

Appendix A

- Amps, kWhs and die temperature during the pelleting process (Alchemy Technology)

Appendix B

- Further OSRS data at alternative ERs

Appendix C

- Miscanthus results at similar ER

Appendix A

Amount of amps and die temperature during manufacturing of OSRS pellets

Pellet type	Amps (A)	Die temperature (^oC)
1	58	74
2	61	85
3	49	63
4	51	66
5	86	97
6	80	92
7	72	81
8	71	78

Assuming a 230 V of electricity supply and duration of all the experiments 90 minutes the energy required by the pellet mill to process 100 kg for each type is:

Pellet type	Energy spent (kWh/100 kg)
1	20
2	21
3	16.9
4	17.6
5	29.7
6	27.6
7	24.8
8	24.5

Appendix B

Performance of the 5 mm oilseed rape straw pellets in a spouted fluidsed bed gasifier within the ER range: 0.28-0.35

		OSRS pellet type					
		1	2	2	3	3	4
Biomass feed (kg/h)		6(1)	7(2)	7(2)	7(2)	6(1)	7(2)
Air feed (l/min)		175(3)	175(3)	200(4)	175(3)	175(3)	175(3)
Equivalence ratio		0.32	0.28	0.31	0.3	0.35	0.3
Average gas composition	CO	7.18	7	5.8	2.95	2.5	4.8
	CO_2	17.3	17.7	17.2	15.7	16.2	16.2
	H_2	3.1	2.45	1.73	0.54	0.5	0.98
	CH_4	1.83	1.86	1.37	0.4	0.38	0.93
	N_2	70.59	70.99	73.9	80.41	80.42	77.09
Gas yield ($m^3/kg_{biomass}$)		1.97	1.68	1.84	1.48	1.73	1.54
HHV (MJ/m^3)		2.03	1.94	1.5	0.6	0.53	1.1
LHV (MJ/m^3)		1.89	1.81	1.4	0.58	0.5	1.04
Cold gas efficiency (%)		20.9	17.1	14.6	4.8	4.8	9
Carbon conversion efficiency (%)		49.4	42.7	42.9	28.5	33	34
CO/CO_2 ratio		0.415	0.4	0.337	0.189	0.154	0.296
Mass conversion factor		0.39	0.34	0.29	0.073	0.092	0.16
Specific energy rate (MJ/m^2*h)		1335	1270	1078	350	305	663
Gasification rate (kg/m^2*h)		117	120	102	26	28	57

(1)Error (SD): ±0.375kg
(2)Error (SD): ±0.37kg
(3)Error: <5%, ±8.75 l/min
(4)Error: <5%, ±10 l/min

Performance of the 18 mm oilseed rape straw pellets in a spouted fluidised bed gasifier within the ER range: 0.15-0.2

		OSRS pellet type				
		5	5	6	7	8
Biomass feed (kg/h)		8.5(1)	11(2)	11(2)	8.5(1)	8.05(3)
Air feed (l/min)		150(4)	150(4)	150(4)	125(5)	125(5)
Equivalence ratio		0.19	0.15	0.15	0.176	0.2
Average gas composition	CO	6.75	7.7	9	8.7	12
	CO_2	16.5	17.1	17.1	17.5	16.6
	H_2	3.1	4.1	5.1	6.3	9.7
	CH_4	1.7	2	3.3	2.6	3.95
	N_2	71.95	69.1	65.5	64.9	57.75
Gas yield ($m^3/kg_{biomass}$)		1.17	0.94	1	1.08	1.28
HHV (MJ/m^3)		1.94	2.3	3.1	2.95	4.32
LHV (MJ/m^3)		1.8	2.15	2.9	2.72	3.98
Cold gas efficiency (%)		11.9	11.4	16	16.4	28.7
Carbon conversion efficiency (%)		27.9	24.2	28	31.6	45.7
CO/CO_2 ratio		0.41	0.45	0.526	0.497	0.72
Mass conversion factor		0.196	0.2	0.25	0.28	0.4
Specific energy rate (MJ/m^2*h)		1074	1340	1900	1516	2490
Gasification rate (kg/m^2*h)		84	110	140	120	170

(1)Error (SD): ±0.336kg
(2)Error (SD): ±0.529kg
(3)Error (SD): ±0.318kg
(4)Error: <5%, ±7.5 l/min
(5)Error: <5%, ±6.25 l/min

Appendix C

Performance of E-On Miscanthus pellets in a spouted fluidised bed gasifier with similar ER

		E-On Miscanthus pellets test No			
		1	2	3	4
Biomass feed (kg/h)		7.3(1)	7.6(1)	7.6(1)	7.6(1)
Air feed (l/min)		150(2)	150(2)	150(2)	150(2)
Equivalence ratio		0.3	0.29	0.29	0.29
Average gas composition	CO	17	16	16.9	15.3
	CO_2	13.5	13.7	13.2	13.7
	H_2	12.2	10.2	11.7	10.8
	CH_4	3.87	3.7	3.4	3.3
	N_2	53.43	56.4	54.8	56.9
Gas yield ($m^3/kg_{biomass}$)		1.83	1.67	1.7	1.65
HHV (MJ/m^3)		5.24	4.8	5	4.6
LHV (MJ/m^3)		4.85	4.4	4.6	4.3
Cold gas efficiency (%)		50.8	42.4	45.3	40.5
Carbon conversion efficiency (%)		75.6	66.9	69	64.1
CO/CO_2 ratio		1.26	1.17	1.28	1.12
Mass conversion factor		0.595	0.5	0.529	0.476
Specific energy rate (MJ/m^2*h)		3915	3391	3625	3241
Gasification rate (kg/m^2*h)		235	206	217	195

(1)Error (SD): ±0.403kg
(2)Error: <5%, ±7.5 l/min